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ACTIVITY AND RELATED THERMODYNAMIC QUANTITIES; THEIR DEFINITION, AND VARIATION WITH TEMPERATURE AND PRESSURE

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The behavior of chemical systems can be simply expressed in terms of a thermodynamic quantity called chemical potential; in theory as well as in practice¹ the chemical potential is of great utility, a large number of the laws of physical chemistry depending directly or indirectly on relations involving this quantity, as shown in detail by Gibbs (6). In the application of the relations to actual measurements there have appeared to be certain difficulties in computation and presentation. Especially in very dilute solutions, or in gases at low pressures, the chemical potential may be inconvenient to tabulate, and the results do not easily give a clear picture of the change in properties of the solution as the concentration varies. Presumably for this reason various substitutes for chemical potential have been proposed and widely used, notably activity, activity coefficient, and osmotic coefficient. These are functions of the chemical potential (or of the partial molal free energy) and are readily obtained from it. For most concentrated solutions it has seemed to some investigators that the advantage of these derived quantities is questionable. The writer in some recent work (2) on the properties of solutions and systems under high pressures, involving much computation of thermodynamic data, came to the conclusion (1) that for such purposes the chemical potential was as convenient as any other function.

On the other hand, we should not lose sight of two important considerations, first, that the introduction of the function, activity, proved a powerful stimulus to the use of thermodynamics by physical chemists, and second, that today activity and related quantities, rather than chemical potential and partial molal free energy, serve as the usual medium for expressing the results of thermodynamic measurements on solutions. This is strikingly evident from a survey of current articles on the subject in

¹ For example, in the determination of solubility curves in systems under pressure by graphical analysis of the chemical potential of a given component in the various phases.

various journals. If, for example, we count the pertinent entries in the index of *Chemical Abstracts* for 1934 (the most recent available at the time this is written) we shall find references to one hundred and three papers. The number of entries for activity is eleven, for activity coefficient forty-three, for chemical potential three, for thermodynamic potential one, and for free energy forty-five. Of the one hundred and three papers, sixty-one are concerned with solutions, eight using chemical potential or partial molal free energy, and fifty-three activity or activity coefficient.

But whether in the study of solutions we prefer to deal with the classical chemical potential (partial free energy), or with the newer functions such as activity, or whether we number ourselves among the very few who do not object to using the one or the other as occasion may arise, it is important to have the interrelations in unambiguous form and to be able to avoid uncertainties in the interpretation of thermodynamic data expressed in any of the commonly accepted units.

The writer's attention was directed toward this subject in utilizing some measurements on solutions for determining the effect of pressure on activity coefficient. Now that the experimental methods for such measurements have been developed, much interesting information will probably be obtained, allowing us to observe how the various well-known solution laws apply to solutions confined at pressures of 10,000 atmospheres or more. It has seemed worthwhile to reexamine critically the definition of activity (as well as other related quantities) and to put it in an equivalent form that is more amenable to the common mathematical operations such as differentiation. This, together with a correlation of the temperature and pressure coefficients of five related thermodynamic functions, is the object of the present communication.

DEFINITIONS

Activity

The activity of a pure substance, or of a specified component in a solution, is commonly defined (13, 15) in either of two ways: (1) in terms of the previously defined² fugacity (12, 16), the activity of the material or component being the ratio of its fugacity in the given state to that in some "standard state"; or (2) by the relation

$$F_2 - F_2^0 = RT \ln a_2 \quad (1)$$

² For a critique of Lewis' definition of fugacity see G. Tunell (J. Phys. Chem. **35**, 2885-913 (1931)), who showed that the fugacity as used by Lewis and Randall (15) is rigorously defined by their equation 14 (Chap. XVII, p. 195), whereas it cannot be defined mathematically by their equation 2 (Chap. XVII, p. 191) and the equations $P^* = f^*$ when $P^* = 0$ (Chap. XVII, p. 193).

in which a_2 denotes the activity of component 2, T the absolute temperature, R the gas constant, \bar{F}_2 the partial molal free energy (i.e., the chemical potential per mole), and \bar{F}_2^0 the value of \bar{F}_2 in the "standard state." Equation 1 is also applicable to a pure substance, the subscripts then merely identifying the material. While \bar{F}_2 and a_2 are functions of temperature, pressure, and concentration, \bar{F}_2^0 is by definition a function only of T . It may be noted that for the standard state, $\bar{F}_2 = \bar{F}_2^0$ and by equation 1 $a_2 = 1$. (\bar{F}_2^0 is considered further in the following paragraph.) It is also important to note that the numerical value of \bar{F}_2 involves an arbitrary molecular weight or formula weight. The assumed molecular weight is a part of the definition of activity; in order to avoid ambiguity we should write

$$\bar{F}_2 = M_2 \mu_2 \quad (2)$$

M_2 being the value taken for the molecular weight, and μ_2 being the chemical potential per gram.

The definition of activity is usually completed by giving more particulars concerning the state designated as "standard." This may be done in a number of ways; for example, by letting this state refer to such a concentration that the ratio of activity to molality approaches unity as the solution becomes more and more dilute. That is,

$$\lim_{m \rightarrow 0} \frac{a_2}{m} = 1 \quad (3a)$$

in which m denotes the molality (moles per 1000 grams of solvent). By definition this relation holds at any temperature but only at $P = 1$. It should be noted, however, that an activity may be defined (22) in such a way that the above limit turns out to be unity at all pressures.

Let us suppose that an arbitrary value of \bar{F}_2^0 be inserted in equation 1, and that from the a_2 so obtained the value of the limit in equation 3a is taken. Then if the limit turns out to be finite, although not unity, it can be readily made equal to unity by an appropriate change in \bar{F}_2^0 . But it is important to note at this point that *a priori* there is no necessity for the limit ever to have a finite value; whether it is finite or not is a matter to be decided by experiment or analogy. Lest this seem to be an item of no consequence we may observe that unless one particular value is assigned to the formula weight, M_2 (for a given solute), the limiting value of a_2/m will either vanish or be infinitely great.

In order to demonstrate that the limit can be finite, it is sufficient to show that the limiting ratio of $e^{(\bar{F}_2 - k)/RT}$ to m is finite (k being a constant). For solutes that do not dissociate Gibbs (7) gave an equation for the approximate relation in dilute solutions between the potential and the con-

centration (i.e., the mass, m_2 , of component 2 divided by the total volume, V). The later form of the equation, in which Gibbs utilized a generalization due to van't Hoff, is as follows:

$$M_2\mu_2 - \text{const.} = RT \ln \frac{m_2}{V} \quad (4)$$

and this equation has been verified by experiment. At low concentrations m_2/V is nearly proportional to m . Therefore, since $M_2\mu_2 = \bar{F}_2$, the ratio of $e^{(\bar{F}_2 - k)/RT}$ to m has a finite limiting value; and consequently the limit in equation 3a is also finite.

But although for a large variety of solutes there can be found a concentration for the standard state such that equation 3a will hold, it will be observed in the case of dissociable substances, such as strong electrolytes, that equation 3a in the form given will not hold with any possible "standard state." The equation must then be modified by raising m to the power, ν , thus,

$$\lim_{m \rightarrow 0} \frac{a_2}{Bm^\nu} = 1 \quad (3b)$$

ν being the number of parts or ions into which one molecule of the substance is assumed to dissociate. The factor, B , which is a constant for the given substance, is inserted arbitrarily for a reason explained in a later section; it is defined by the relation

$$B = (\nu_+)^{\nu_+}(\nu_-)^{\nu_-} \quad (5)$$

in which ν_+ and ν_- are the number of the two kinds of ions. Activities based on mole fractions, $(a_2)_x$, and on volume concentrations, $(a_2)_c$, have also been used, and may be evaluated by substituting X_2 , the mole fraction of component 2, or C , the number of moles of component 2 per 1000 cc. of solution, for m in equation 3b. The relation between a_2 and $(a_2)_x$ is obviously,

$$\frac{(a_2)_x}{a_2} = \frac{1}{N_1'} \quad (6a)$$

N_1 being the number of moles in 1000 grams of component 1 (solvent).

Similarly the relation between a_2 and $(a_2)_c$ is

$$\frac{(a_2)_c}{a_2} = \rho_0^\nu \quad (6b)$$

ρ_0 being the density of pure liquid 1. Concentrations have been expressed (9) in terms of the "modified mole fraction," Y_2 , calculated on the basis

of the solute being completely dissociated. We may also define an activity, $(a_2)_r$, in terms of Y_2 , and we have

$$\frac{(a_2)_r}{(a_2)_x} = \nu' \quad (6c)$$

If we were to concern ourselves only with solutions of components miscible in all proportions, the definition of activity could be made much simpler; for in that event the "standard state" (in this instance the concentration to which \bar{F}_2^0 pertains) could be—but does not need to be—taken as the pure component under consideration. In mixtures of water and ethyl alcohol, for example, the activity of the alcohol could be evaluated by using the pure alcohol as the fiduciary, or standard, state; equations 3a and 3b and the limiting behavior in dilute solutions would not then be involved in the definition.

The majority of solutions for which thermodynamic data exist show limited miscibility, and even in those that show complete miscibility it may be preferred to reckon always from one end of the diagram. In general, therefore, the definition of activity has required two equations, for example 1 and 3a. It is obvious that a single equation would be more convenient for mathematical treatment.

Now equation 1 defines a_2 except for an arbitrary multiplicative constant and equation 3 defines the constant. This circumstance led to the following single equation for defining activity.

$$a_2 = \lim_{m' \rightarrow 0} \frac{m'}{e^{(\bar{F}'_2 - \bar{F}_2)/RT}} \quad (7a)$$

For simplicity we have taken first the special case of a solute that does not dissociate. The equation is applied (at a given temperature and pressure) by choosing any concentration, m , and determining $\bar{F}'_2 - \bar{F}_2$, for a series of concentrations, m' , keeping m , and consequently \bar{F}_2 , constant, and then finding by graphical or other means the limiting value toward which the ratio on the right hand of the equation tends as m' approaches zero. Substituting this limiting value in equation 7a we find a_2 at the concentration m . Here \bar{F}'_2 pertains to a fixed pressure, that is, $P = 1$. This is equivalent to the statement that \bar{F}_2^0 is always to be taken at $P = 1$. It may be noted that although Lewis and Randall specify that the standard state of a pure liquid, and also that of a solute, is always taken at unit pressure, a similar definite statement is not made for the solute. The assumption here made is that the activities of solute and solvent are to be defined on the same basis.

The operation of evaluating the limit as m approaches zero is analogous to the operation of evaluating a definite integral. Here m' and \bar{F}'_2 play

the part of variables, and m (or \bar{F}_2) is a parameter corresponding to one of the limits of the integral. Moreover, the determination of the limit in equation 7a is implied by, and presupposed in, Lewis' definition; and the evaluation of the limit has in effect been carried out whenever a_2 has been determined. In applying this equation at various temperatures and pressures (if it is to conform to Lewis' definition of activity) we must observe that \bar{F}_2 is a function of T and P , and that \bar{F}_2' is a function of T but not of P .

That equation 7a is equivalent to the two equations, 1 and 3a, which have previously been used to define activity, may be readily shown. We may write equation 7a in the form,

$$a_2 = e^{\bar{F}_2/RT} \lim_{m' \rightarrow 0} \frac{m'}{e^{\bar{F}_2'/RT}} \quad (8)$$

Then for any a_2 (the limit itself being constant) we have, after taking logarithms,

$$RT \ln a_2 = \bar{F}_2 - \text{const.} = \bar{F}_2 - \bar{F}_2^0$$

since \bar{F}_2^0 is the value of the constant for which $a_2 = 1$. Equation 7a thus leads to an equation identical with equation 1. Furthermore, by dividing equation 7a by m and taking the limit as m approaches zero, we have (at $P = 1$, since in that event one limit is the reciprocal of the other),

$$\lim_{m \rightarrow 0} \frac{a_2}{m} = \left(\lim_{m \rightarrow 0} \frac{e^{\bar{F}_2/RT}}{m} \right) \left(\lim_{m' \rightarrow 0} \frac{m'}{e^{\bar{F}_2'/RT}} \right) = 1$$

which is identical with equation 3a.

Equation 7a may readily be put in the more general form applicable to all classes of solutes. Thus

$$a_2 = B \lim_{m' \rightarrow 0} \frac{(m')^\nu}{e^{(\bar{F}_2' - \bar{F}_2)/RT}} \quad (7b)$$

in which, as before, $B = \nu_+^{*+} \cdot \nu_-^{*-}$. By following the same procedure as for equation 7a it may be readily shown that equation 7b is equivalent to the two equations (1 and 3b) used in the general definition of activity. Here, also, \bar{F}_2 is a function of T and P , and \bar{F}_2' is a function of T but not of P . For purposes of this definition ν may be regarded as that number which will give a finite value for the limit. With a larger number the limit is zero and with a smaller number it is infinite. Experimentally it will be found that ν is a small positive integer, and is usually in agreement with the number of parts into which, from other considerations, the component is known to dissociate.

In many instances the quantity directly measured is the difference between \bar{F}_2 at a concentration m , and \bar{F}_2'' at some fixed arbitrary reference concentration. Equation 7b may be put in a slightly different form, which is more directly applicable to the data from which a_2 is usually determined. Inserting $e^{(\bar{F}_2'' - \bar{F}_2'')/RT} (= 1)$ in equation 7b, and making use of the fact that (at $P = 1$) the value of the limit involving only \bar{F}_2' and m' as variables is the same as that of the limit involving only \bar{F}_2 and m as variables, we have

$$a_2^{1/\nu} = B^{1/\nu} \frac{e^{(\bar{F}_2 - \bar{F}_2'')/RT}}{\lim_{m \rightarrow 0} \frac{e^{(\bar{F}_2 - \bar{F}_2'')/RT}}{m}} \quad (9)$$

In determining the value of the limit by graphical means it is convenient in the case of strong electrolytes to plot the ratio (whose limit is sought) against \sqrt{m} , because at low concentrations a nearly straight line will be obtained. This equation is primarily suitable for calculating a_2 at some fixed temperature and at one atmosphere pressure. For variations in T and P , the quantity \bar{F}_2'' , and also the quantities determining the limit, must be taken at the given temperature but at a fixed pressure.

If it is desired to work with logarithms rather than exponentials, we can alter equation 9 by taking the logarithms of both sides. But it should be noted that a limiting *ratio* is often less troublesome to work with than the limiting *difference* that occurs in the altered equation. In order to define $(a_2)_x$, the activity based on mole fractions, X_2 or X_2' may be substituted for m or m' respectively, in equations 7, 8, and 9; similarly, $(a_2)_c$ may be defined by the equations after substituting C and C' for m and m' .

These equations may be easily applied by an appropriate choice of subscripts to any component in a solution, the limiting composition, and its distinguishing sign, corresponding to one of the pure (liquid) components; and the equations readily take the simpler form that suffices for defining the activity of a component, when the component itself in pure liquid form is chosen as the limiting state (10). If we write the analog of equation 7a or 7b with X_1' in place of m' , the limit being taken as X_1' approaches one, and note that here \bar{F}_1' has the finite limiting value \bar{F}_1^* (the value of \bar{F}_1 for pure component 1) we obtain an equation, similar to equation 1,

$$a_1 = e^{(\bar{F}_1 - \bar{F}_1^*)/RT} \quad (10)$$

for completely defining the activity in this instance. The above equations may be made more general by using a generalized subscript instead of the numerals 1 and 2, which have been used above in order to emphasize the fact that more care is needed in the definition and evaluation of the activity

of the solute than in the case of the solvent. A more general form of definition than equation 7b is,

$$a_i = B \lim_{x_i \rightarrow x} \frac{(X'_i)'}{e^{(\bar{F}'_i - \bar{F}_i)/RT}} \quad (7c)$$

The question sometimes arises as to whether, in the case of electrolytes, the activity, a_2 , refers to the undissociated solute or to the dissociated part, or to something else. In order to avoid confusion it should be carefully noted that, inasmuch as a_2 (at a fixed T and P) is proportional to e^{μ_2} , and inasmuch as μ_2 is simply the chemical potential of one gram of the solute, then a_2 for, say, sodium chloride, as commonly used and as defined above, may be regarded as merely the activity of a solute whose condition is not qualified except by the statement that its gross composition (in this instance) corresponds to the formula NaCl. It may be noted, however, that a_2 is equal to, or proportional to, the activity of the undissociated part, and to the geometric mean of the ion activities.

Activity coefficient

As usually defined, the activity coefficient, γ , of a given solute (at $P = 1$) bears the following relation to the activity, a_2 , of the same component,

$$\gamma = \frac{a_2^{1/\nu}}{B^{1/\nu} m} \quad (\text{at } P = 1) \quad (11)$$

From equation 3b it is evident that γ , defined in this way, approaches 1 as a limit, as m approaches zero. Instead of defining γ in terms of the previously defined a_2 , we may define it directly in terms of \bar{F}_2 . Upon combining equations 7b and 11, we have

$$m\gamma = \lim_{m' \rightarrow 0} \frac{m'}{e^{(\bar{F}'_2 - \bar{F}_2)/\nu RT}} \quad (12)$$

Since this was obtained from equation 10 (with \bar{F}'_2 having the meaning specified in equation 7b), γ , by equation 3b, approaches 1 as a limit only at $P = 1$. Now, from the pressure coefficient of a_2 (see below) it is evident that a more general form of equation 3b is

$$\lim_{m \rightarrow 0} \frac{a_2^{1/\nu}}{B^{1/\nu} m} = e^{I/\nu RT} \quad (\text{at any } P) \quad (13)$$

in which I is written for the integral $\int_1^P \bar{V}_2^* dP$, \bar{V}_2^* being the limiting value of the partial molal volume of component 2. Since we wish to have γ

approach 1 at all pressures, we therefore divide the right-hand side of equation 12 by $e^{I/\nu RT}$. This is equivalent to adding $I/\nu RT$ to \bar{F}'_2 , which originally was always at $P = 1$, and thus changing \bar{F}'_2 to the value it would have at the given pressure. Hence in order to define γ so that for any pressure it approaches 1 as m approaches zero, we merely specify that in equation 12 \bar{F}'_2 , as well as \bar{F}_2 , is a function of P . That is, \bar{F}_2 and \bar{F}'_2 are both taken at the given pressure and temperature.

For actual calculation of γ a somewhat more convenient form is obtained by combining equations 9 and 11. Thus,

$$\gamma = \frac{e^{(\bar{F}_2 - \bar{F}'_2)/\nu RT}}{\lim_{m \rightarrow 0} \frac{e^{(\bar{F}_2 - \bar{F}'_2)/\nu RT}}{m}} \quad (14)$$

By reasoning similar to that employed in connection with equation 11 it follows that here \bar{F}_2 and \bar{F}'_2 are both functions of T and P . Of the two equations, equation 12 is the simpler, but equation 14 is the more generally useful; it is directly applicable to measurements of $\bar{F}_2 - \bar{F}'_2$, such as those obtained from the E.M.F.'s of concentration cells without liquid junctions, by use of the well-known relation, $\bar{F}_2 - \bar{F}'_2 = n\mathbf{F}\mathbf{E}$, in which \mathbf{E} is the E.M.F. of the cell in volts, \mathbf{F} is the number of energy units (e.g., calories) per volt equivalent, and n is the number of equivalents associated with the particular formula weight, M_2 , that is used in connection with \bar{F}_2 . The sign of $\bar{F}_2 - \bar{F}'_2$ can be kept correct by recalling that \bar{F}_2 always increases algebraically with the concentration of component 2.

The operation of finding the value of the limit in equation 14 is analogous to that used by Lewis and Randall (17) in connection with their equation XXVI-15 for calculating γ from \mathbf{E} . If we take the natural logarithm of the limit and multiply by $-\nu RT/n\mathbf{F}$ we obtain the quantity designated as \mathbf{E}^0 by Lewis and Randall.

Other kinds of activity coefficient of the solute, such as

$$\gamma_{X_2} (= (a_2)^{1/\nu} / B^{1/\nu} X_2)$$

based on mole fractions, or $\gamma_C (= (a_2)^{1/\nu} / B^{1/\nu} C)$, based on volume concentration, have been used, and can be defined by substituting X_2 or C , respectively, for m in the above equations. The interrelations of these various activity coefficients may be readily obtained. If the analog of equation 12, containing X_2 in place of m , and γ_{X_2} in place of γ , be written, and the one equation divided by the other, we obtain

$$\frac{X_2 \gamma_{X_2}}{m \gamma} = \lim_{\substack{X_2' \rightarrow 0 \\ m' \rightarrow 0}} \frac{X_2'}{m'} = \frac{1}{N_1} \quad (15)$$

(N_1 being the number of moles of solute in 1000 grams). Thence,

$$\gamma_{x_2} = \gamma \left(1 + \frac{m}{N_1} \right) = \frac{\gamma}{X_1} \quad (16a)$$

Similarly, it follows directly that

$$\gamma_c = \gamma \frac{m}{C} \rho_0 = \gamma \frac{\rho_0}{x_1} \quad (16b)$$

in which ρ and ρ_0 are the densities of solution and solute and x_1 is the weight fraction of the solvent. We may also define γ_{Y_2} ($= (a_2)_{Y_2}^{1/\nu} / B^{1/\nu} Y_2$) by substituting Y_2 for m in equation 12, and we have,

$$\gamma_{Y_2} = \gamma_{x_2} \nu \frac{X_2}{Y_2} \quad (16c)$$

Although it is the activity coefficient of the dilute component (solute) that is the most useful one in actual practice, the activity coefficient of the solvent (or in general the activity coefficient of any component in a solution) may be similarly defined in terms of the activity of the component and its concentration. If component 1 is the solvent, then both X_1 and a_1 , as defined by equation 10, approach unity in dilute solution. Therefore any power of a_1 , divided by any power of X_1 , might be chosen as the activity coefficient, for example of water in an aqueous solution. The natural choice would seem to be a_1/X_1 , and this coefficient is the one commonly used (11). But it should be noted that in general $(a_2)_x$ becomes nearly equal to X_2^ν in dilute solution; whence by the well-known relation connecting a_1 and a_2 it follows that in dilute solution a_1 is more nearly proportional to X_1^ν than to X_1 . Accordingly the activity coefficient, γ_{x_1} , of the solvent will be defined by the equation,

$$\gamma_{x_1} = \frac{a_1^{1/\nu}}{X_1} = \frac{e^{(\bar{r}_1 - r_1^*)/\nu RT}}{X_1} \quad (17)$$

This of course includes the special case for which $\nu = 1$. It may seem strange that the definition of the activity coefficient of the solvent should involve the factor ν , which is entirely a property of the solute. But as a matter of fact the definition does not need to involve ν ; putting in the ν as indicated in equation 17 merely makes the γ_{x_1} , so defined, more nearly equal to unity (as a rule), and causes the relations between γ_{x_1} and other quantities such as osmotic coefficient (see below) to be more simple than they otherwise would be.

An activity coefficient of the solvent based on Y_1 , the "modified mole fraction," has also been used (9, see also 8). The Y_1 is calculated from

the known weight of the constituents by taking the (mean) molecular weight of the solute as $1/\nu$ of the formula weight used in calculating X_1 . The activity coefficient γ_{r1} is then defined as

$$\gamma_{r1} = \frac{a_1}{Y_1} \quad (18)$$

When X_1 is nearly equal to 1, X'_1 is approximately equal to Y_1 ; from which it may be shown that $\gamma_{X'_1}$ and γ_{r1} have nearly the same numerical values for dilute solutions, although they differ appreciably for higher concentrations. The exact and approximate relations between these two varieties of activity coefficient of the solvent are as follows:

$$\frac{\gamma_{X'_1}}{\gamma_{r1}} = \frac{Y_1}{X'_1} \doteq 1 + \frac{\nu(\nu-1)}{2} \left(\frac{X_2}{X_1}\right)^2 - \frac{\nu(\nu^2-1)}{3} \left(\frac{X_2}{X_1}\right)^3 \quad (19)$$

Alternate definition of activity

By Lewis' definition of activity a_2/m^ν does not in general approach unity as a limit as m approaches zero, even at $P = 1$; it does so only for di-ionic electrolytes or non-dissociable substances (ν equal to 1 or 2). This is because Lewis, for strong electrolytes, writes $a_+^\nu \cdot a_-^\nu/a_2$ as an equilibrium constant involving the activities of the individual ions and adopts the arbitrary convention (20) that the equilibrium constant is equal to 1. Now, the activities of the individual ions may be taken as sensibly equal to ν_+m and ν_-m , respectively, at high dilutions, and therefore $a_+^\nu \cdot a_-^\nu$ at atmospheric pressure will approach Bm^ν as a limit as m approaches zero. Hence, by the above convention as to equilibrium constant, a_2 approaches Bm^ν as a limit (which is in accord with equation 3b); and the factor B thus enters into the definition of a_2 .

But it would be better for many purposes to define an activity in such a way that the factor B would be omitted. This could be done by adopting the convention that $a_+^\nu \cdot a_-^\nu/a_2$ equals B rather than 1. If this were done, a_2 at high dilutions would approach the limit Bm^ν/B , or m^ν . That is,

$$\lim_{m \rightarrow 0} \frac{[a_2]}{m^\nu} = 1 \quad (\text{at } P = 1) \quad (20)$$

in which we put $[a_2]$ for the quantity that bears a simple relation to a_2 , the activity as ordinarily defined (being identical with a_2 when ν is 1 or 2). Since $[a_2] = Ba_2$, we may now omit the B in the fundamental definition of activity, and write

$$[a_2] = \lim_{m' \rightarrow 0} \frac{(m')^\nu}{e^{(\bar{F}_1' - \bar{F}_1)/RT}} \quad (21)$$

by analogy with equation 7a. Here, as before, \bar{F}_2 is a function of P and T , and \bar{F}_2' a function of T but not of P . It is thus possible to define a useful variety of solute activity, in terms of measurable quantities, without any reference to the activities or properties of individual ions, ν as stated above being merely that number which gives the limit a finite value. The only disadvantage of the alternate definition is that $[a_2]$ is less simply related to the activities of the individual ions, and this is offset by the greater simplicity of the relation between $[a_2]$ and γ .

As is evident from equation 11, γ may be defined independently of any convention regarding a_2 ; hence the value of γ is not affected by the suggested change in the definition of activity.

We have, moreover,

$$[a_2^{1/\nu}] = m\gamma, \quad [a_2^{1/\nu}]_x = X_2\gamma_{x_2}, \quad [a_2^{1/\nu}]_c = C\gamma_c, \quad [a_2^{1/\nu}]_r = Y_2\gamma_{r_2} \quad (22)$$

(at $P = 1$), and instead of the usual equation,

$$\bar{F}_2 - \bar{F}_2^0 = \nu RT \ln (m\gamma) + RT \ln B \quad (23)$$

we have the simpler equation,

$$\bar{F}_2 - [\bar{F}_2^0] = \nu RT \ln (m\gamma) \quad (24)$$

in which $[\bar{F}_2^0]$ pertains to a "standard state" for which not only $[a_2]$ but also $m\gamma$ is equal to 1.

Osmotic coefficient

A now familiar thermodynamic function is the osmotic coefficient, introduced by Bjerrum (3) and originally defined in terms of osmotic pressure. For any solution, f_P , the osmotic coefficient of the solute, may be defined as the ratio of π , the osmotic pressure of the solution, to what the osmotic pressure would be if the solution followed some ideal-solution law; that is,

$$f_P = \frac{\pi}{\pi_{id}} \quad (25)$$

The numerical value of f_P thus depends on the particular ideal law that is chosen.

Osmotic pressure and chemical potential (partial free energy) are connected by the well-known exact relation,

$$\Delta\bar{F}_1 = \bar{F}_1 - \bar{F}_1^* = -(\bar{V}_1)_0\pi + I_\nu \quad (26)$$

in which \bar{F}_1 and \bar{F}_1^* are the partial molal free energies (at atmospheric pressure) of component 1 and of pure liquid 1, respectively, $(\bar{V}_1)_0$ is the fictive

volume per mole of component 1 in the given solution at atmospheric pressure, and I_v is given by

$$I_v = - \int_1^{\pi} \Delta_P \bar{V}_1 dP$$

$\Delta_P \bar{V}_1$ being the difference between the value of \bar{V}_1 at any pressure P and that at atmospheric pressure.³ From equation 26 it is evident that the ideal-solution law employed to determine π_{id} also determines $(\Delta \bar{F}_1)_{id}$, the value of $\Delta \bar{F}_1$ in the hypothetical solution that follows the chosen ideal law. We have, then,

$$(\Delta \bar{F}_1)_{id} = -(\bar{V}_1)_0 \pi_{id} + (I_v) \quad (27)$$

in which (I_v) is written for the integral taken between the limits 1 and π_{id} .

From equations 25, 26, and 27 it follows that

$$f_P = \frac{-\Delta \bar{F}_1 + I_v}{-(\Delta \bar{F}_1)_{id} + (I_v)} \quad (28)$$

The osmotic coefficient, f_P , can thus be defined in terms of measurable quantities and an arbitrary assumption as to the course of either π or $\Delta \bar{F}_1$ in an ideal solution. Therefore in order to complete the definition of f_P , we may choose an ideal law for $\Delta \bar{F}_1$.

For the sake of convenience it is preferable to have a "law" that does not deviate too much from the actual measurements, and it is necessary that in dilute solution $(\Delta \bar{F}_1)_{id}$ should approach $\Delta \bar{F}_1$ if the limiting value of f_P is to be 1. Although there are a number of relations that may serve the purpose, there appears to be no simple relation that is entirely satisfactory for all classes of solutions. The most convenient one for many purposes is,

$$(\Delta \bar{F}_1)_{id} = -\nu RT \frac{m}{N_1} \quad (29)$$

The well-known expression that includes Raoult's law and puts $\Delta \bar{F}_1$ equal to $RT \ln X_1$ is not even approximately true for solutions of electrolytes, dilute or concentrated; but a slight modification makes it more generally applicable. Thus, if we write

$$(\Delta \bar{F}_1)_{id} = \nu RT \ln X_1 \quad (30)$$

³ For the special case of constant compressibility, or more exactly, of linear variation of \bar{V}_1 with P , the term $(\bar{V}_1)_0 \pi - I_v$ becomes equal to π times the value of V_1 at $P/2$. See reference 11, pp. 109, 120.

the equation conforms fairly well to the actual course of \bar{F}_1 in very dilute solutions of electrolytes; and for non-electrolytes (ν then being equal to 1) it reduces to the familiar form. Another expression nearly equivalent to equation 30 in dilute solutions is

$$(\Delta\bar{F}_1)_{id}'' = RT \ln Y_1 \quad (31)$$

Y_1 being the "modified" mole fraction (see above).

If we choose equation 29 for our ideal-solution law, then by equations 25, 26, and 28 we have

$$f_P = \frac{(\bar{V}_1)_0 \pi}{\nu RT m / N_1 + (I_v)} = \frac{-\Delta\bar{F}_1 + I_v}{\nu RT m / N_1 + (I_v)} \quad (32)$$

Other choices of ideal law would, of course, lead to different expressions and to different numerical values of f_P .

Now, I_v is usually small in comparison with the terms to which it is added. For example, $-\Delta\bar{F}_1$ for a 4.277 molal solution of sodium chloride in water at 25°C. is 103.8 cal., $\nu RT m / N_1$ is 91.3 cal., π is 243.8 bars (calculated from $\Delta\bar{F}_1$), and I_v is 0.6 cal. The fact that I_v is small suggests that another variety of osmotic coefficient⁴ might be defined by the equation,

$$f_r = \frac{-\Delta\bar{F}_1}{\nu RT m / N_1} \quad (33)$$

It is evident that when, as is approximately so in sufficiently dilute solutions, equation 29 represents the variation of $\Delta\bar{F}_1$ with m , f_r will be 1. For the purpose of defining f_r , the factor ν may be regarded as that number (usually an integer) which will make f_r tend toward unity in dilute solution.

Since I_v and (I_v) are nearly proportional to π^2 and π_{id}^2 , respectively, an approximate relation between f_r and f_P may be obtained by combining equations 32 and 33. Thus,

$$f_P \doteq f_r + \frac{I_v}{-\Delta\bar{F}_1} (f_r - 1) \quad (34)$$

For π less than 1000 bars the difference between f_P and f_r is less than can be determined by any method that has been used for measuring $\Delta\bar{F}_1$. The two coefficients, f_P and f_r , become strictly identical for an incompressible solution ($I_v = 0$). Moreover, if not only $I_v = 0$, but $\bar{V}_1 = v_1$, the molal volume of the pure solvent, and if the ideal-solution law is

⁴ Called the "osmotic coefficient for the chemical potential" by Scatchard and Prentiss (J. Am. Chem. Soc. **56**, 1486-92 (1934)).

equation 29, then it follows that $[\pi_{id}]'$, the osmotic pressure under the specified conditions, would be

$$[\pi_{id}]'V = \nu N_2 RT \quad (35)$$

in which V denotes the total volume of the solution and N_2 denotes the total number of moles of solute. This is the van't Hoff equation in more general form (5) on account of the inclusion of the factor ν , and indicates that if an osmotic coefficient were defined as $\pi V/\nu N_2 RT$ this coefficient would, under the assumed restriction (incompressibility and no volume change on mixing), be identical with f_r .

Equation 30 suggests the definition of a third well-known kind of osmotic coefficient, thus,

$$f_x = \frac{\Delta \bar{F}_1}{\nu RT \ln X_1} \quad (36)$$

By combining equations 34 and 36 and expanding $\ln X_1$, the relation between f_r and f_x may be expressed as follows,

$$\frac{f_r}{f_x} = \frac{-\ln X_1}{m/N_1} = 1 - \frac{m}{2N_1} + \frac{m^2}{3N_1^2} - \dots \quad (37)$$

Again, a coefficient f_r may be defined by the equation,

$$f_r = \frac{\Delta \bar{F}_1}{RT \ln Y_1} \quad (38)$$

and we have,

$$\frac{f_r}{f_y} = 1 - \frac{\nu m}{2N_1} + \frac{\nu^2 m^2}{3N_1^2} - \dots \quad (39)$$

Still another common way of defining an osmotic coefficient⁵ is in terms of the freezing-point depression, which by well-known thermodynamic equations is directly related to the osmotic pressure of the solution. Let us define f by

$$f = \frac{\vartheta}{\vartheta_{id}} \quad (40)$$

in which $\vartheta \equiv T_0 - T'$ (T_0 being the freezing point of the pure solvent and T' that of the solution), and ϑ_{id} is determined by some ideal-solution law.

⁵ We might also define an osmotic coefficient in terms of C , the volume concentration or molality, by substituting C for m in equation 33.

The familiar equation for freezing-point lowering in a dilute solution may be expressed as follows,

$$\lim_{\vartheta \rightarrow 0} -\frac{dT'}{dm} = \nu \frac{RT_0^2}{N_1 \Delta H_0} = \nu \lambda \quad (41)$$

in which R is the gas constant, N_1 as before is the number of moles of solvent in 1000 grams, ΔH_0 is the heat *absorbed* in the melting of one mole of solvent at T_0 , and λ is a factor defined by the second part of the equation ($\lambda = 1.858$ for aqueous solutions). Now, ϑ_{fd} is conveniently defined as $m(dT/dm)_0$, that is, $\nu \lambda m$; whence

$$f = \frac{\vartheta}{\nu \lambda m} = \frac{\vartheta \Delta H_0}{\nu R T_0^2 m / N_1} \quad (42)$$

In order to write an expression for the exact relation between f and one of the other osmotic coefficients, we first note the equation given by Lewis and Randall (18) for connecting $\Delta \bar{F}_1$ and ϑ . This is

$$-(\Delta F_1)' = \vartheta \left(\frac{\Delta H_0}{T_0} - \vartheta \frac{\Delta C_P}{2T_0} - \vartheta^2 \frac{\Delta C_P}{6T_0^2} \right) \quad (43)$$

which is equivalent to

$$-\ln(a_1)' = \frac{1}{N_1 \lambda} \vartheta + b \vartheta^2 + c \vartheta^3 + \dots \quad (44)$$

Here

$$b = \left(\frac{\Delta H_0}{T_0} - \frac{\Delta C_P}{2} \right) / R T_0^2, \quad c = \left(\frac{\Delta H_0}{T_0} - \frac{2\Delta C_P}{3} \right) / R T_0^2$$

and ΔC_P (assumed constant) is the molal heat capacity of the pure liquid solvent minus that of the solid. For aqueous solutions, $\Delta H_0/T_0 = 1438$ cal. per degree, $\Delta C_P = 9$, $b = 5.16 \times 10^{-6}$, $c = 1.8 \times 10^{-8}$.

When ϑ for a given concentration has been determined, equations 43 and 44 give $\Delta \bar{F}_1$ and a_1 for that concentration and at a temperature equal to the freezing point of the particular solution. The $\Delta \bar{F}_1$'s obtained in this way from a series of ϑ 's thus pertain to various temperatures. Now, f_r may be calculated from $\Delta \bar{F}_1$ by equation 33, which involves also the temperature T , and we designate by the symbols $(f_r)'$, $(\Delta F_1)'$, and $(a_1)'$ those values pertaining not to a single fixed temperature but to a temperature that for each concentration is T' ($= T_0 - \vartheta$). We have, then, by equations 33 and 43,

$$(f_r)' = \frac{\vartheta \left(\frac{\Delta H_0}{T_0} - \vartheta \frac{\Delta C_P}{2T_0} - \vartheta^2 \frac{\Delta C_P}{6T_0^2} \right)}{\nu R T m / N_1} \quad (45)$$

and by equation 42

$$\frac{(f_r)'}{f} = \frac{T_0}{T'} \left(1 - \frac{\Delta C_P}{2\Delta H_0} \vartheta - \frac{\Delta C_P}{6T_0\Delta H_0} \vartheta^2 \right) \quad (46)$$

Noting that $T_0/T' = 1/(1 - \vartheta/T_0)$, expanding and neglecting terms containing ϑ^3 and higher powers of ϑ , we obtain finally

$$\frac{(f_r)'}{f} = 1 + bN_1\lambda^2\nu fm + cN_1\lambda^3\nu^2f^2m^2 \quad (47)$$

The last term in this equation can usually be neglected, and we then have for aqueous solutions,

$$\frac{(f_r)'}{f} = 1 + 0.00099 \nu fm \quad (47a)$$

Equation 47a is practically the same as that given by Scatchard and Prentiss (21). Equation 47 can be put in the following form,

$$f = (f_r)' - \frac{bN_1\vartheta^2}{\nu m} - \frac{cN_1\vartheta^3}{\nu m} \quad (48)$$

In order to pass from $(f_r)'$ to f_r we may make use of the equation given below for calculating the variation of f_r with temperature. It should be noted that whereas f_r, f_X, f_Y , and f_P are functions of T , f and $(f_r)'$ are not. All six of these quantities (by definition) approach 1 as a limit as the concentration of the solute decreases. At $m = 0.01$ they are practically identical, but at higher concentrations they differ appreciably among themselves. For example, f for a 4.277 molal sodium chloride solution in water is 1.042, $(f_r)'$ is 1.051, and at 25°C., f_r, f_X, f_Y , and f_P are respectively 1.137, 1.180, 1.223, and 1.138.

Relation between activity coefficients and osmotic coefficients

By equation 23 and the well-known equation connecting \bar{F}_1 and \bar{F}_2 we have (at constant temperature and pressure),

$$- \frac{N_1}{m} d\bar{F}_1 = d\bar{F}_2 = \nu RT d \ln (m\gamma) \quad (49)$$

Then from equation 33 it follows that

$$d(f_r m) = m d \ln (m\gamma) = m d \ln \gamma + dm \quad (50)$$

This equation, in slightly different form, has been given by Bjerrum (4).

Integrating (temperature and pressure being constant), we obtain

$$f_r = 1 + \frac{1}{m} \int_1^\gamma m d \ln \gamma = 1 + \ln \gamma - \frac{1}{m} \int_0^m \ln \gamma dm \quad (51)$$

since $f_r = 1$ and $\gamma = 1$, when $m = 0$. This is an exact relation between f_r and γ at any concentration and at a given constant T and P .

An equation resembling equation 51 but involving f rather than f_r may also be written. By equation 49, we have,

$$-\frac{N_1}{m} d \ln a_1 = d \ln a_2 = \nu d \ln (m\gamma) \quad (52)$$

and by differentiating equation 44, the last term being neglected, we obtain

$$-d \ln (a_1)' \doteq \frac{1}{N_{1\lambda}} d\vartheta + 2b\vartheta d\vartheta \quad (53)$$

Now, equation 52 gives the relation between a_1 and γ at a fixed temperature. Nevertheless we may apply the first and last terms to connect $(a_1)'$, which is the activity at the varying temperature T' , with a number, $(\gamma)'$, which is not the activity coefficient but becomes equal to it if a_1 is independent of T . Combining this modification of equation 52 with equation 53 and with the differential form of equation 42 we obtain,

$$d \ln (m\gamma)' \doteq \frac{d(fm)}{m} + \frac{2bN_{1\vartheta}d\vartheta}{\nu m} \quad (54)$$

and, by integration,

$$f \doteq 1 + \frac{1}{m} \int_1^{\gamma'} m d \ln (\gamma)' - \frac{bN_{1\vartheta}^2}{\nu m} \quad (55)$$

A closer approximation can of course be obtained by not neglecting the term containing ϑ^2 in equation 44.

For aqueous solutions bN_1 is equal to 0.000286. Equation 54 is essentially the equation given by Lewis and Randall (19) for connecting $(\gamma)'$ with the function j , which is closely related to f (see below). In general γ differs from $(\gamma)'$,—by an amount that depends on the heat of dilution. In moderately dilute solutions this effect becomes inappreciable and $(\gamma)'$ is then (sensibly) equal to γ . By subtracting equation 48 from equation 55 it may be observed that

$$(f_r)' = 1 + \frac{1}{m} \int_1^{\gamma'} m d \ln (\gamma)' \quad (56)$$

The exact relation between f_x and γ_{x_2} is easily obtained. Since

$$-\frac{X_1}{X_2} d\bar{F}_1 = d\bar{F}_2 = \nu RT d \ln (X_2\gamma_{x_2}) \quad (57)$$

we have, by applying equation 36,

$$d(f_x \ln X_1) = -\frac{X_2}{X_1} d \ln (X_2 \gamma_{x_2}) \quad (58)$$

or, by integration,

$$f_x = 1 - \frac{1}{\ln X_1} \int_1^{\gamma_{x_2}} \frac{X_2}{X_1} d \ln \gamma_{x_2} \quad (59)$$

Furthermore, the relation between γ_{x_1} , the activity coefficient of the solvent, and its osmotic coefficient, f_x , is obtained by combining equations 17 and 36. Thus

$$\ln \gamma_{x_1} = (f_x - 1) \ln X_1 \quad (60)$$

These and other interrelations between activity coefficients and osmotic coefficients have been given previously, for example by Guggenheim (reference 11, p. 107), who has also pointed out that in dilute solutions the activity coefficient of the solvent differs from unity by a much smaller quantity than does the osmotic coefficient. This is immediately evident from the approximate form of equation 60, obtained by expanding $\ln X_1$:

$$\gamma_{x_1} = 1 + (1 - f_x)X_2 \quad (61)$$

Since in dilute solutions both X_2 and $1 - f_x$ are small quantities, it follows that $\gamma_{x_1} - 1$ has a magnitude that is one order smaller than $1 - f_x$. For example in a 0.01 molal sodium chloride solution at ordinary room temperature f_x is 0.9703 and γ_{x_1} is 1.00000535. In general, for dilute solutions, if $1 - \gamma_{x_2}$ is proportional to $X_2^{\frac{1}{2}}$ or X_2 , then $1 - f_x$ is proportional to $X_2^{\frac{1}{2}}$ or X_2 , respectively, and $\gamma_{x_1} - 1$ is proportional to $X_2^{\frac{1}{2}}$ or X_2^2 , respectively. Moreover, $1 - \gamma_{x_2}$, $1 - f_x$, and $\gamma_{x_1} - 1$ have the same sign (usually positive in dilute solutions for electrolytes and negative for non-electrolytes).

It is of interest to note that the factor ν in the more general definitions of γ_{x_2} , f_x , and γ_{x_1} does not appear in the transformation equations. On the other hand, for the activity coefficient, a_1/X_1 , in dilute solutions we have the following approximate relation,

$$\frac{a_1}{X_1} = 1 - (\nu f_x - 1) X_2 \quad (62)$$

The Lewis and Randall function, j

This was devised (14) as an aid in the calculation of activity coefficients from freezing-point measurements. It is defined in terms of ϑ , the freezing-point lowering, as follows:

$$j = 1 - \frac{\vartheta}{\nu \lambda m} \quad (63)$$

(ν being 1 for a non-dissociable solute) and is closely related to one of the several varieties of osmotic coefficients. From equation 42 it is obvious that

$$j = 1 - f \quad (64)$$

This function, like f , readily determines $(\Delta\bar{F}_1)'$ for a given concentration at the temperature T' , the freezing point of the particular solution. By the same procedure used with f it follows that, to a sufficient approximation,

$$j \doteq -\frac{1}{m} \int_1^{\gamma'} m \, d \ln (\gamma)' + \frac{bN_1\vartheta^2}{\nu m} \quad (65)$$

which is one form of Lewis and Randall's equation, and connects j with $(\gamma)'$, the "uncorrected activity coefficient." Since j is uniquely determined by $(\Delta\bar{F}_1)'$, it may properly be called a thermodynamic function.

Other functions

The van't Hoff mole number (23) is the ratio of the magnitude of some effect, such as freezing-point depression, osmotic pressure, or vapor-pressure lowering, to the effect expected from an arbitrary ideal-solution or dilute-solution law applied to an undissociated substance with the assumed molecular weight. The effect most commonly used is that involved in equations 41 and 42 with ν equal to 1, namely, $\vartheta = \lambda m$. Accordingly the mole number, i , may be defined by the equation,

$$i = \frac{\vartheta}{\lambda m} \quad (66)$$

It follows that

$$i = \nu f \quad (67)$$

and from equation 55 that

$$i \doteq \nu + \frac{\nu}{m} \int_1^{\gamma} m \, d \ln (\gamma)' - \frac{bN_1\vartheta^2}{m} \quad (68)$$

For a solute that does not dissociate i is identical with f ; but of course the mole number is ordinarily used only in connection with electrolytes.

It is also worthwhile to include in our list of the thermodynamic functions, frequently employed in the study of solutions, the Arrhenius dissociation factor α . This is the classical "degree of dissociation" and is commonly defined in terms of the mole number i . For a di-ionic electrolyte α is put equal to $i - 1$, and in general is defined by the equation,

$$\alpha = \frac{i - 1}{\nu - 1} \quad (69)$$

From equations 55 and 67 we have an equation connecting α and $(\gamma)'$,

$$\alpha \doteq 1 + \frac{\nu}{(\nu - 1)m} \int_1^{\gamma'} m \, d \ln (\gamma)' - \frac{bN_1 g^2}{(\nu - 1)m} \quad (70)$$

Defined in this way i and α are thermodynamic functions in the same sense and for the same reason that the osmotic coefficient f is a thermodynamic function. For a solution of any specified concentration, the mole number i determines $(\Delta \bar{F}_1)'$ at T' and, if the heat of dilution is known, $\Delta \bar{F}_1$ at any temperature. The same applies to α , which, it may be noted, can not be used if $\nu = 1$. The conductance ratio, also designated sometimes by the symbol α , bears no exact relation to the α here defined, although in many instances the two factors are strikingly similar in magnitude.

It is interesting to compare the four quantities: α , the Arrhenius dissociation factor; i , the van't Hoff mole number; f , (one form of) the Bjerrum osmotic coefficient; and j , the Lewis and Randall function—each of which has played an important part in the development of physical chemistry. Their interrelation may be summarized as follows

$$(\nu - 1) (1 - \alpha) = \nu - i = \nu (1 - f) = \nu j \quad (71)$$

VARIATION WITH TEMPERATURE

Activity

When once the definition of a quantity has been formulated it is usually a simple matter to differentiate the function with respect to temperature and thus to find its temperature coefficient. An exception to this rule is found in activity as ordinarily defined. If we attempt to find da_2/dT at constant concentration by taking the derivative of equation 1, we at once run into difficulty. This is because \bar{F}_2^0 (for the solute), in general, pertains to a different concentration for each temperature. Solutions of the problem have been obtained by utilizing the two equations (1 and 3) of the complete definition of a_2 , an essential part of which is a statement concerning the limiting behavior of a_2 in an infinitely dilute solution. Although the correct answer has been given, it appears that the methods used for deriving the expression for the change with temperature of the activity of the solute have proved troublesome for many serious students of the subject.

On the other hand, the single equation (7b) for defining activity is easily amenable to rigorous mathematical treatment. For determining the temperature coefficient of a_2 at constant composition and pressure we note first that the operation of taking the limit is associative with respect to the other common mathematical operations, as illustrated by the

well-known rule that "the limit of a product is the product of the limits," and second, the familiar relation between \bar{F}_2 and T :

$$\frac{d(\bar{F}_2/T)}{dT} = -\frac{\bar{H}_2}{T^2} \quad (\text{constant } m \text{ and } P) \quad (72)$$

\bar{H}_2 being the fictive enthalpy (per mole) of component 2 (that is, $(\partial H_2/\partial N_2)_{T, P, N_1}$, H_2 being the enthalpy, or heat content, and N_1 and N_2 the total number of moles of component 1 and 2, respectively). We note also that \bar{F}_2 and \bar{F}_2' in equation 7 are functions of T , and that the limit refers to a series of values of m' that may be taken to be the same at all temperatures; m' is not a function of T . Taking the derivative of equation 7b we have

$$\begin{aligned} \frac{da_2}{dT} &= B \lim_{m' \rightarrow 0} \frac{(m')'(\bar{H}_2' - \bar{H}_2)/RT^2}{e^{(\bar{F}_1' - \bar{F}_2)/RT}} \\ &= a_2 \lim_{m' \rightarrow 0} \frac{\bar{H}_2' - \bar{H}_2}{RT^2} \end{aligned}$$

Let the limiting value of \bar{H}_2 , as m' approaches zero, be \bar{H}_2^* . (By experiment it is known that $(\bar{H}_2' - \bar{H}_2)$ has a finite and readily determinable limit.) Then,

$$\frac{d \ln a_2}{dT} = -\frac{\bar{H}_2 - \bar{H}_2^*}{RT^2} \quad (\text{const. } P \text{ and } m) \quad (73)$$

It might possibly have been somewhat simpler to take the logarithm of both sides of equation 7b before taking the derivative. The derivative of $\ln(a_2)_x$, of $\ln(a_2)_c$, and of $\ln(a_2)_r$ will be found to be the same as that of $\ln a_2$. By changing subscripts in equation 73 we obtain $d \ln a_1/dT$ (also at constant composition and pressure). The quantity \bar{H}_1^* that occurs here is the molal enthalpy (heat content) of the pure solvent.

Activity coefficient

The variation of γ with temperature offers comparatively little difficulty; it may be obtained in a variety of ways, for example by taking the derivative of equation 12, which yields the expression,

$$\frac{d \ln \gamma}{dT} = -\frac{\bar{H}_2 - \bar{H}_2^*}{\nu RT^2} \quad (\text{const. } P \text{ and } m) \quad (74)$$

and the same for $d \ln \gamma_{x_2}/dT$, for $d \ln \gamma_{r_2}/dT$, and for $d \ln \gamma_c/dT$. Similarly, from equation 17,

$$\frac{d \ln \gamma_{x_1}}{dT} = -\frac{\bar{H}_1 - \bar{H}_1^*}{\nu RT^2} \quad (\text{const. } P \text{ and } m) \quad (75)$$

and the same for $d \ln \gamma_{r_1} / dT$, except that the ν is omitted. The "uncorrected" activity coefficient, $(\gamma)'$, can not be considered a function of T .

Osmotic coefficient

The variation of f_r with temperature, obtained by taking the derivative of equation 33, may be expressed as follows:

$$\frac{df_r}{dT} = \frac{\bar{H}_1 - \bar{H}_1^*}{\nu RT^2 m / N_1} \quad (\text{const. } P \text{ and } m) \quad (76)$$

If $\Delta \bar{C}_{P1}$ is the (constant) difference between the fictive molal heat capacity of the component 1 and the pure solvent, then the integrated form of equation 76 is,

$$\begin{aligned} \frac{\nu R m}{N_1} (f_r - (f_r)') = & - \left(\frac{\Delta \bar{F}_1}{T} - \frac{(\bar{F}_1)'}{T'} \right) = \left(\frac{(\Delta \bar{H}_1)_T}{T} - \Delta \bar{C}_{P1} \right) \frac{T - T'}{T'} \\ & + \Delta \bar{C}_{P1} \ln \frac{T}{T'} \pm \frac{(\Delta \bar{H}_1)_T}{T} \frac{\theta}{T} + \left(\frac{(\Delta \bar{H}_1)_T}{T} - \frac{\Delta \bar{C}_{P1}}{2} \right) \frac{\theta^2}{T^2} \\ & + \left(\frac{(\Delta \bar{H}_1)_T}{T} - \frac{2 \Delta \bar{C}_{P1}}{3} \right) \frac{\theta^3}{T^3} \end{aligned} \quad (77)$$

in which $\theta = T - T'$ and $(\Delta \bar{H}_1)_T = \bar{H}_1 - \bar{H}_1^*$ at T . Equation 77 is in convenient form for calculating f_r at a fixed temperature T , when $(f_r)'$ at a given temperature T' is known. Incidentally the equation closely resembles equation 44. It may be noted that the determination of γ from f (or from i , j , or α) would involve the calculation of $(f_r)'$ by equation 47 or 48, the calculation of f_r by equation 77, and the calculation of γ by equation 51.

From equation 36 we obtain the expression, similar to that for f_r ,

$$\frac{df_x}{dT} = - \frac{\bar{H}_1 - \bar{H}_1^*}{\nu RT^2 \ln X_1} \quad (78)$$

The equation for df_r/dT is of the same form (without the ν). An expression for df_r/dT can be written, but it is somewhat complicated. The other variety of osmotic coefficient, f , is not a function of temperature; the same applies to i , j , and α .

VARIATION WITH PRESSURE

Activity

The change of a_2 with P (at constant m and T) can be obtained from equation 7, or still more easily from equation 1, since by definition \bar{F}_2^0 is not a function of P ,—which accounts for the fact that the variation with

P is more simple in form than the corresponding variation with T . We have then (since $d\bar{F}_2/dP = \bar{V}_2$),

$$\frac{d \ln a_2}{dP} = \frac{\bar{V}_2}{RT} \quad (\text{const. } m \text{ and } T) \quad (79)$$

and the same expression for $(a_2)_x$, $(a_2)_c$, or $(a_2)_r$. The quantity \bar{V}_2 is the fictive volume of component 2 (per mole). Similarly, from equation 10 we have,

$$\frac{d \ln a_1}{dP} = \frac{\bar{V}_1}{RT} \quad (\text{const. } X_1 \text{ and } T) \quad (80)$$

Activity coefficient

From equation 12 we obtain,

$$\frac{d \ln \gamma}{dP} = \frac{\bar{V}_2 - \bar{V}_2^*}{\nu RT} \quad (\text{const. } m \text{ and } T) \quad (81)$$

This may be put in the integrated form,

$$\ln \gamma = (\ln \gamma)_{P=1} + \frac{1}{\nu RT} \int_1^P \Delta_x \bar{V}_2 dP \quad (82)$$

Here \bar{V}_2^* is the limiting value of \bar{V}_2 as m approaches zero, and $\Delta_x \bar{V}_2$ is written for $\bar{V}_2 - \bar{V}_2^*$ at any pressure, P . The same expression is obtained when γ_{x2} , γ_{r2} , or γ_c is substituted for γ .

It is well known that if, as is true for strong electrolytes in dilute solution, $\ln \gamma = -\omega m^\dagger$ (ω being a function of T and P but not of m) then $\bar{H}_2 - \bar{H}_2^*$ is proportional to m^\dagger and $\bar{H}_1 - \bar{H}_1^*$ is equal to $-m(\bar{H}_2 - \bar{H}_2^*)/3N_1$. From this it follows that for such solutions $(\partial \ln \gamma / \partial T)_{P,m} = 3(\partial f_r / \partial T)_{P,m}$. This relation is in agreement with, and might have been derived from, the relation shown by Lewis and Randall (reference 15, p. 346) to exist at low concentrations between $\ln \gamma$ and j , which in dilute solutions is approximately equal to $1 - f_r$.

From equation 10 we have also

$$\frac{d \ln \gamma_{x1}}{dP} = \frac{\bar{V}_1 - \bar{V}_1^*}{\nu RT} \quad (\text{const. } X_1 \text{ and } T) \quad (83)$$

On the other hand, for the other varieties of activity coefficient (of the solvent), a_1/X_1 and γ_{r1} , we have equations similar to equation 83 except that the ν is omitted.

Osmotic coefficient

The change of f_r and of f_x with P is obtained directly from equations 33 and 36, respectively. Thus

$$\frac{df_r}{dP} = -\frac{\bar{V}_1 - \bar{V}_1^*}{\nu RTm/N_1} \quad (\text{const. } m \text{ and } T) \quad (84)$$

and

$$\frac{df_x}{dP} = \frac{\bar{V}_1 - \bar{V}_1^*}{\nu RT \ln X_1} \quad (\text{const. } X_1 \text{ and } T) \quad (85)$$

The equation for df_r/dP is obtained by replacing $\nu \ln X_1$ by $\ln Y_1$.

It may be noted that by experiment it has been found that for all types of solutes the limit of $(\bar{V}_1 - \bar{V}_1^*)/m$, as m approaches zero, is zero. This is in accord with the definition of f_r , by which f_r has the limiting value 1 at all pressures. In dilute solutions of strong electrolytes it is known that $\bar{V}_2 - \bar{V}_2^*$ is proportional to $m^{1/2}$; whence, $\bar{V}_1 - \bar{V}_1^*$ is equal to $-m(\bar{V}_2 - \bar{V}_2^*)/3N_1$, and $(\partial \ln \gamma / \partial P)_{T,m} = 3(\partial f_r / \partial T)_{T,m}$ for such solutions.

The derivative of f_P with respect to P can not be written, because from the method of defining it f_P can not be considered a function of P . If f_P were defined (more generally) on the basis of an osmotic pressure, π , measured from P as a starting point, then f_P obviously would depend on P , and df_P/dP would have a meaning.

Since f is a function of $(\Delta \bar{F}_1)'$ it is also a function of P —although not of T , because $(\Delta \bar{F}_1)'$ is at a predetermined temperature. An expression for df/dP can be obtained, but the complete equation is rather complicated, and it will suffice, for the present, to note that in dilute solutions, or whenever $\bar{H}_1 - H_1^*$ is negligible, f is nearly equal to f_r and therefore

$$\left(\frac{\partial f}{\partial P} \right)_m \doteq -\frac{\Delta_x \bar{V}_1}{\nu RTm/N_1} \quad (\text{approx., in dilute solution}) \quad (86)$$

Under the same conditions a similar expression can be written for the variation of i , j , and α with pressure.

SUMMARY

It is shown that activity may be defined by a single equation equivalent to the two equations of the usual definition. This equation is easily amenable to mathematical operations such as differentiation.

It is furthermore suggested that activity be defined so as to omit the factor $\nu_+^+ \cdot \nu_-^-$ that appears in the customary definition of the activity of an electrolyte.

Several varieties of activity coefficient, osmotic coefficient, and other

related functions are in common use. A number of these are defined and correlated, and their derivatives with respect to temperature and pressure are given.

REFERENCES

- (1) ADAMS, L. H.: J. Am. Chem. Soc. **53**, 3769-813 (1931), footnote on p. 3797.
- (2) ADAMS, L. H.: J. Am. Chem. Soc. **53**, 3769-813 (1931). See also ADAMS, L. H.: J. Am. Chem. Soc. **54**, 2229-43 (1932) and ADAMS, L. H., AND GIBSON, R. E.: J. Am. Chem. Soc. **54**, 4520-37 (1932).
- (3) BJERRUM, N.: Fysisk Tids. **15**, 66 (1916); Z. Elektrochem. **24**, 321-8 (1918); Z. anorg. Chem. **109**, 275-92 (1920).
- (4) BJERRUM, N.: Z. physik. Chem. **104**, 406-32 (1923).
- (5) See FALKENHAGEN, H.: Electrolytes, p. 39. Translation by R. P. Bell. Oxford (1934).
- (6) GIBBS, J. W.: Scientific Papers, Vol. 1, pp. 55-353. Longmans, Green and Co., London (1906).
- (7) Reference 6, pp. 137, 420, 426.
- (8) GIBSON, R. E., AND ADAMS, L. H.: J. Am. Chem. Soc. **55**, 2679-95 (1933).
- (9) GILBAUT: Z. physik. Chem. **24**, 385-440 (1897).
- (10) GORANSON, R. W.: Thermodynamic Relations in Multi-component Systems. Carnegie Inst. Wash. Pub. No. 408, p. 325 (1930).
- (11) See, for example, GUGGENHEIM, E. A.: Modern Thermodynamics by the Methods of Willard Gibbs, pp. 104, 125. Methuen and Co., Ltd., London (1933).
- (12) LEWIS, G. N.: Z. physik. Chem. **33**, 205-26 (1901).
- (13) LEWIS, G. N.: Proc. Am. Acad. Arts Sci. **43**, 259 (1907); Z. physik. Chem. **61**, 129-65 (1907).
- (14) LEWIS, G. N., AND RANDALL, M.: J. Am. Chem. Soc. **43**, 1112-54 (1921).
- (15) LEWIS, G. N., AND RANDALL, M.: Thermodynamics and the Free Energy of Chemical Substances, p. 355. McGraw-Hill Book Co., New York (1923).
- (16) Reference 15, p. 190 et seq.
- (17) Reference 15, pp. 266, 334.
- (18) Reference 15, p. 283.
- (19) Reference 15, pp. 286, 347.
- (20) Reference 15, pp. 326, 328.
- (21) SCATCHARD, G., AND PRENTISS, S. S.: J. Am. Chem. Soc. **56**, 1488 (1934).
- (22) SCHOTTKY, W., ULICH, H., AND WAGNER, C.: Thermodynamik, pp. 284, 285. Springer, Berlin (1929).
- (23) VAN'T HOFF, J. H.: Z. physik. Chem. **1**, 481-508 (1887).

THE SYNTHESIS AND STRUCTURE OF BENZOPYRYLIUM (CHROMYLIUM) SALTS

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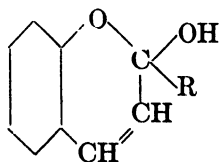
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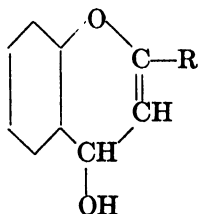
I. SYNTHESIS

A. Introduction

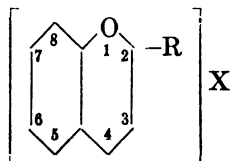
Benzopyrylium salts are salts of the basic benzopyranols (I), usually with mineral acids, which may be isolated as such or as double salts with, for example, ferric chloride. They are represented in this review by the general formula II, except in the discussion of their structure, and the numbering of the substituents is as shown. The salts usually possess a



or



I



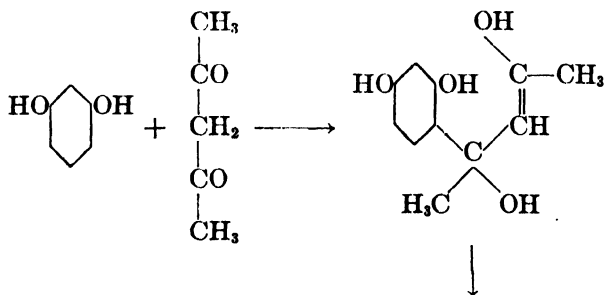
II

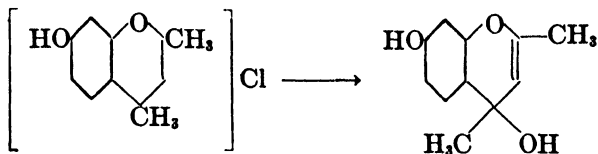
substituent in the 2-position, although unsubstituted salts have been described, as for example, the 3-isopropylbenzopyrylium salts of Decker and Fellenberg (30). When the 2-substituent is a phenyl group the salts are usually referred to as flavylium salts, following the nomenclature of flavones in the chromone series, and Robinson and Walker (103) have recently suggested that, on the same basis, the term "benzopyrylium" should be replaced by "chromylium."

The history of the synthetic salts commences with the conversion by Feuerstein and Kostanecki (40) of salicylidenediacetophenone into 4-phenacylidene-flavene, the anhydro base of the 4-phenacylflavylium salts. The first actual salts were prepared by Bulow and Wagner (18), although their existence had been predicted by Hewitt in the previous year (62). Since their discovery these salts have assumed importance owing to, first, the theoretical speculations they have given rise to with respect to their structure and, second, the researches of Willstätter which established their relationship to the natural anthocyanins. The latter has led to a considerable extension of synthetic methods, notably by Robinson and his collaborators. Reviews of the natural products have already been given by Robinson (98, 99, 100), and it is not proposed to deal with them here except insofar as they affect either the synthetic methods for the production of benzopyrylium salts or the problem of their structure.

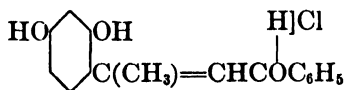
B. The condensation of diketones (or hydroxymethylene ketones) with reactive phenols

This synthesis was introduced by Bulow and his collaborators in an attempt to prepare representatives of the reduction products of the ketone group in chromones (15, 16, 17, 18, 19). They found that the condensation of 1,3-diketones or of 1,3-aldehydoketones with phenols in the presence of a dehydrating agent led to derivatives of substituted 1,4-benzopyranols. The following scheme represents the course of the reaction between acetylacetone and resorcinol in the presence of hydrogen chloride. Similar compounds were also prepared from phloroglucinol and pyrogallol.



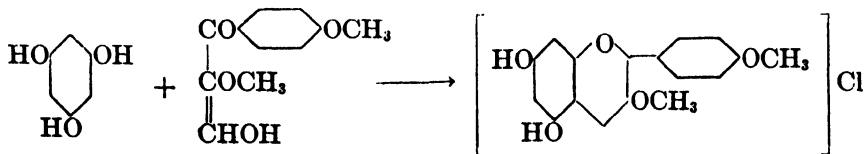


According to Bulow and Wagner (19) the condensation of resorcinol and benzoylacetone in glacial acetic acid solution by means of hydrogen chloride leads to the formation of 4-methyl-7-hydroxyflavylium chloride, which they described as a yellow crystalline solid having one molecule of water of crystallization attached to it. A brownish-yellow, less soluble modification also mentioned was not further investigated. It is apparent that in the case of an unsymmetrical diketone like benzoylacetone two possible products may be formed, namely, 4-methyl-7-hydroxyflavylium chloride and 2-methyl-4-phenyl-7-hydroxybenzopyrylium chloride. Bulow and Wagner established the constitution of their compound by alkaline hydrolysis to acetophenone and resacetophenone. Buck and Heilbron (14), repeating this preparation, found that the product agreeing with that described by Bulow and Wagner contained 0.5 mole of resorcinol so firmly attached that it was not removed by repeated crystallizations. They modified the procedure by replacing the glacial acetic acid by 80 per cent formic acid and thus obtained the salt either anhydrous or containing one mole of water. The difference depended on very small modifications of the procedure. The latter compound, they suggest, may not be a true pyrylium salt but the hydrochloride of the open chain unsaturated ketone (III).



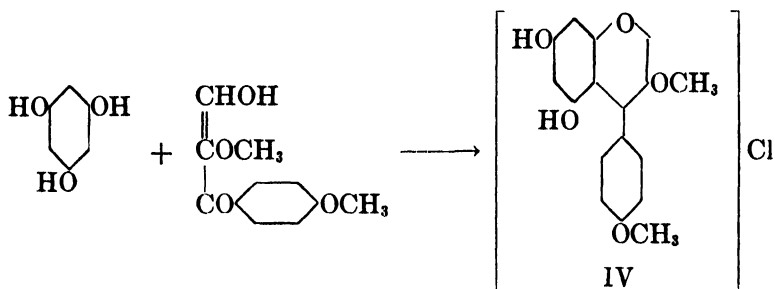
III

In utilizing the reaction for the synthesis of 3,5,7,4'-tetrahydroxyflavylium chloride by the condensation of phloroglucinol and anisyl α -methoxy- β -hydroxyvinyl ketone

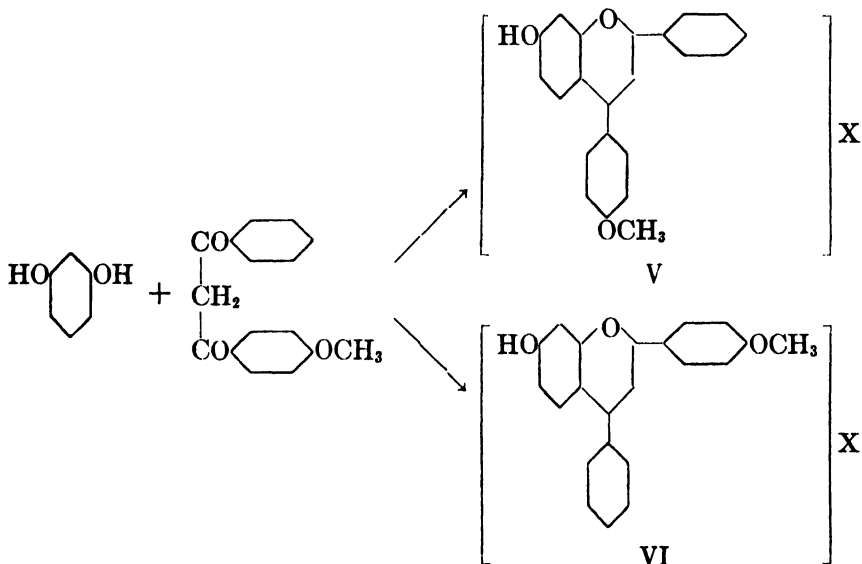


Malkin and Robinson (80) found evidence of what they termed *epi*-

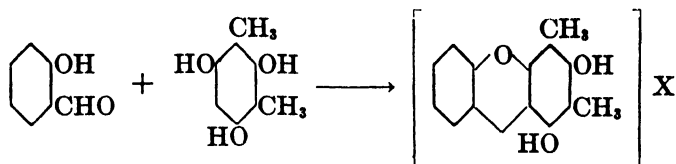
pelargonidin chloride dimethyl ether (IV) formed by condensation as follows.



A further illustration of the caution which must be exercised in the use of this reaction is afforded by a recent paper of Robinson and Walker (102), who found that the condensation of resorcinol and benzoylanisoylmethane results in the formation of a difficultly separable mixture of salts (V and VI).

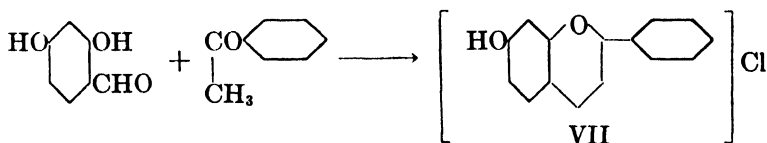


A reaction which may be considered as an extension of Bulow's synthesis was described by Weidel and Wenzel (108). It consists in the condensation of an *o*-hydroxybenzaldehyde with a reactive phenol under the influence of hydrogen chloride to form a xanthylum salt.

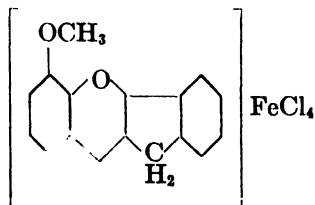


C. The condensation of o-hydroxy aldehydes with ketones

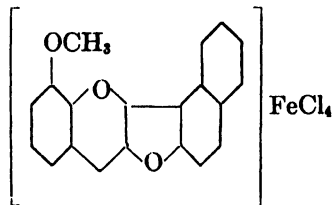
This method for the preparation of benzopyrylium salts was outlined in notes by Decker (26) and Perkin and Robinson (87) and was more fully described in the following years by Decker and Fellenberg (28, 29) and Perkin, Robinson, and Turner (88). It has proved to be one of the most widely used synthetic methods and many modifications of the original synthesis have been introduced. The reaction is typified by the following scheme of the condensation between resorcylic aldehyde and acetophenone which, in the presence of hydrogen chloride, results in the formation of 7-hydroxyflavylum chloride (VII).



Although it breaks down in the case of the simplest flavylum salt, the reaction is capable of very wide application. Both the aldehyde and the ketone appear to be variable at will. As instances of its wide utility may be cited the preparation of such compounds as 8-methoxy-2,3-indeno(1, 2)benzopyrylium ferrichloride (VIII) (101) and 8-methoxy- β -naphthacoumarano-($\beta, \alpha, 2, 3$)benzopyrylium ferrichloride (IX) (95).



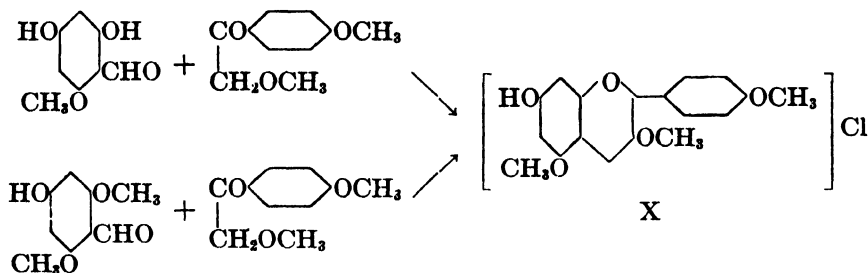
VIII



IX

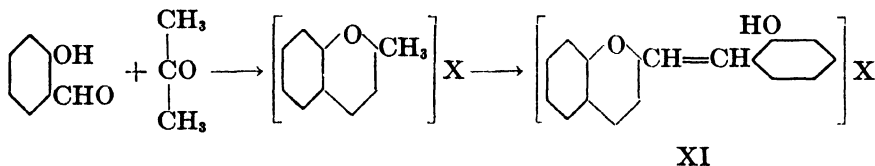
By the employment of ω -substituted acetophenones Robinson and his collaborators have succeeded in preparing numerous 3-substituted flavylum salts related to the naturally occurring anthocyanidins. The vigor of the reaction may be judged from the fact that 7-hydroxy-3,5,4'-tri-

methoxyflavylium chloride (X), which is prepared normally from 2-methylphloroglucinaldehyde, may also be obtained by the same procedure from 2,6-dimethylphloroglucinaldehyde, the latter reaction involving the elimination of the *o*-methyl group.

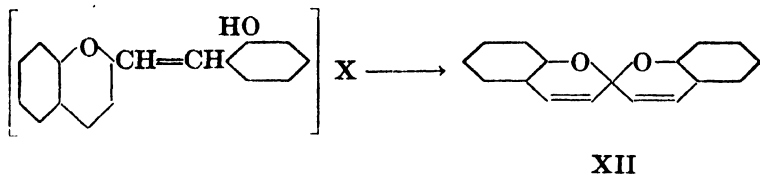


The method is not without its difficulties however. The polyhydroxybenzaldehydes are not easily condensed, and in their earlier synthetic work Pratt and Robinson (92, 93) used the methylated aldehydes and demethylated the subsequent flavylium salts. This procedure had its drawbacks and a search was made for groups that would afford the maximum of protection to the hydroxyl groups combined with the minimum difficulty in their removal. This led to the introduction first of the acetyl derivatives and later of the benzoyl derivatives (see references 95, 96).

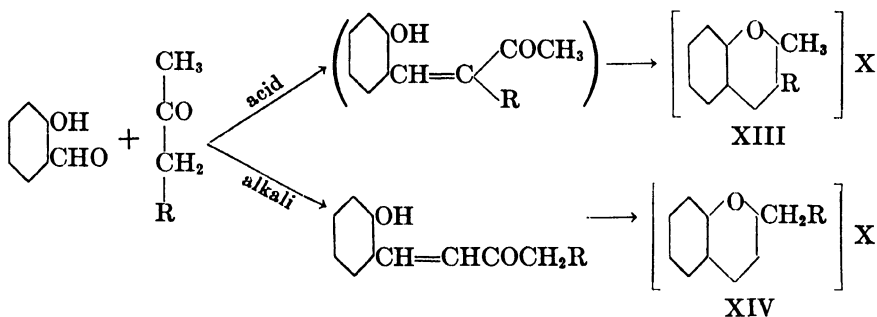
A further difficulty arises in the preparation of the 2-methylbenzopyrylium salts by this method. In this case the desired salt may be accompanied by appreciable quantities of the 2-vinyl derivative (XI) as a result of further condensation between the aldehyde and the reactive 2-methyl group (30, 31, 32, 76).



The latter compounds readily pass over into the corresponding *spiro* pyrans (XII) which, in some instances, may form the sole product of the reaction (30, 32, 104).



As in the case of Bulow's method the reaction may, when the ketone contains both a methyl and a methylene group, proceed in either of two directions. It has generally been accepted that the former or the latter will be reactive towards aldehydes according to whether the condensation is carried out in alkali or acid (6, 46, 47, 55, 56). Thus a ketone of type $\text{CH}_3\text{COCH}_2\text{R}$ would lead to either 2-methyl-3-R- or 2-R-methylbenzopyrylium salts (XIII and XIV) depending on whether it was condensed directly by acid to the salt or indirectly by alkali through the chalcone (see later).



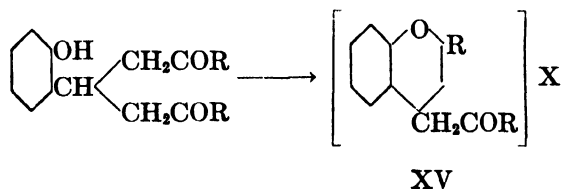
In conformity with this, Decker and Fellenberg (30) prepared 2,3-dimethylbenzopyrylium chloride by direct condensation of methyl ethyl ketone and salicylaldehyde with acid and 2-ethylbenzopyrylium chloride from the same starting materials via the chalcone prepared in alkali.

The generalization cannot be accepted too literally, however, since exceptions to it have been recorded by Stoermer and Wehln (106), Gheorghiu and Arwentiew (45), Lovett and Roberts (78), and Heilbron and Irving (60).

Reference has been made to the preparation of the salts by preliminary condensation of *o*-hydroxy aldehydes and ketones to chalcones which undergo ring closure in the presence of acids. This modification was generalized by Pratt and Robinson (90), and its importance will be apparent from the preceding paragraphs. It provides a method for the isolation in a state of purity of intermediate compounds which can hardly give rise to ambiguous results. Its importance is enhanced by the many solvents which have been suggested for the original condensation with acids. The condensation, which does not invariably proceed smoothly, has often been assisted by a change of solvent. Hence the reaction has been carried out in the absence of solvent, by condensation with concentrated aqueous acids either in the cold or with heating, and in a variety of solvents such as alcohol, ether, glacial acetic acid, formic acid, acetyl

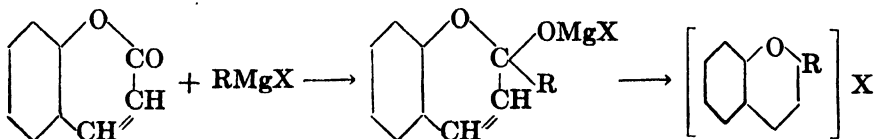
chloride, and ethyl acetate. Of these the most usually employed is glacial acetic acid. The use of some of the others is attended by uncertainties as to the part that they may play in the reaction. Pratt and Robinson (91) found that formic acid, for example, might enter into the condensation, and its use was later generalized for the production of xanthylum salts (57).

The preparation of the chalcones is often accompanied by the formation of *o*-hydroxybenzylidenediketones, and by slight modifications of the procedure the latter can be made the principal products of the reaction (23, 31, 40, 64, 69). Since similar benzylidenediketones without an *o*-hydroxy group can be prepared by the agency of hydrogen chloride (12, 105), it is evident that the condensation of *o*-hydroxy aldehydes and ketones to give benzopyrylium salts may result in the formation of appreciable quantities of the corresponding diketones. Besides diminishing the yield of the desired product, these compounds are capable of forming 4-phenacyl-flavylium salts (XV), which may contaminate the final product (65). This has actually been shown by Hill and Melhuish (66) to occur in the case of the condensation of salicylaldehyde and *p*-methoxyacetophenone in ethereal solution, and the formation of such 4-substituted salts as by-products of the direct condensation cannot therefore be overlooked.

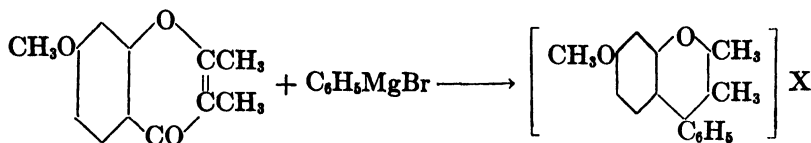


D. The Grignard reaction with benzopyrones

Like the last-described synthesis this procedure was first introduced by Decker (26). Bunzly and Decker (20) had previously found that the action of alkylmagnesium halides on xanthone led to xanthylum salts; the reaction was extended to coumarins and described by Decker and Fellenberg (28, 29) who, by its use, prepared both 2-alkyl- and 2-aryl-benzopyrylium salts. The reaction, generalized in the following scheme, was used by Willstätter for the synthesis of anthocyanidins from 3-methoxycoumarins (113, 114, 115).

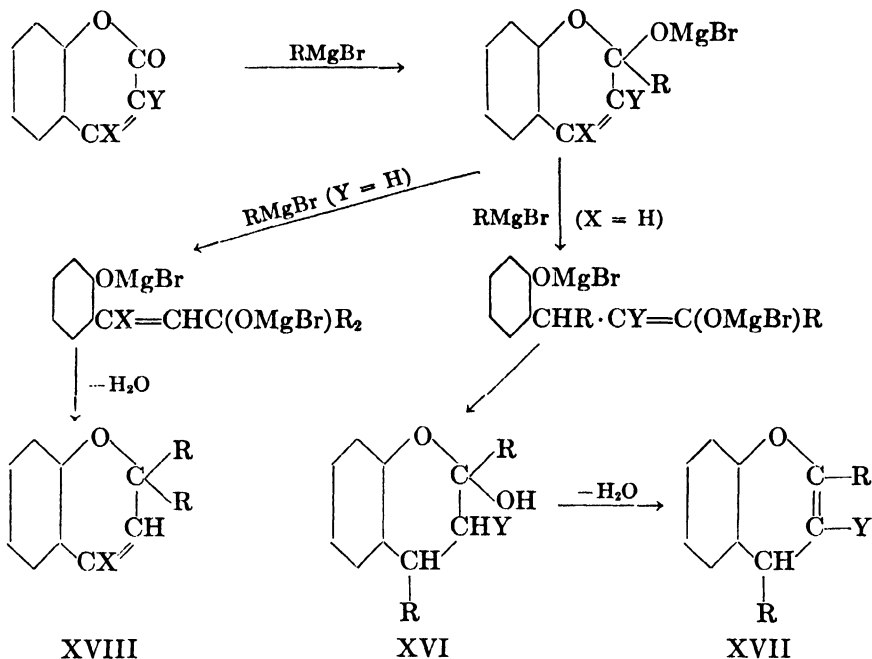


In 1926 Heilbron and Zaki (61) published an extension of the reaction to the preparation of 4-substituted benzopyrylium salts by the interaction of phenylmagnesium bromide and 2,3-dimethyl-7-methoxychromone.



A careful study of this reaction has been made by Löwenbein (75) and by Heilbron and Hill (58). According to Houben (68) the interaction of alkylmagnesium halides and coumarin led to the formation of 2,2-dialkyl- Δ^3 -chromenes, while phenylmagnesium bromide gave rise to a diphenyl-*o*-hydroxystyrylcarbinol. Löwenbein showed that the supposed carbinol of Houben was in reality 2,4-diphenylchroman-2-ol, which can be converted easily by the action of glacial acetic acid into 2,4-diphenyl- Δ^2 -chromene. He also obtained a 2,2-diphenyl- Δ^3 -chromene. Heilbron and Hill then established the conditions under which these compounds were formed. They found that 3-methyl- and 3-phenyl-coumarin both yielded, on treatment with an excess of phenylmagnesium bromide in the hot, the corresponding chromanols (XVI), which were readily dehydrated on heating with glacial acetic acid to the Δ^2 -chromenes (XVII). 4-Methyl- and 4-methoxy-coumarins, on the other hand, yielded under the same conditions 2,2-diphenyl- Δ^3 -chromenes (XVIII), the constitution of which was established by alkaline hydrolysis. These results led to the conclusion that the primary reaction of the Grignard compound followed a common course, the ultimate formation of Δ^2 - or Δ^3 -chromenes being influenced solely by the position of the substituent in the pyrone ring.

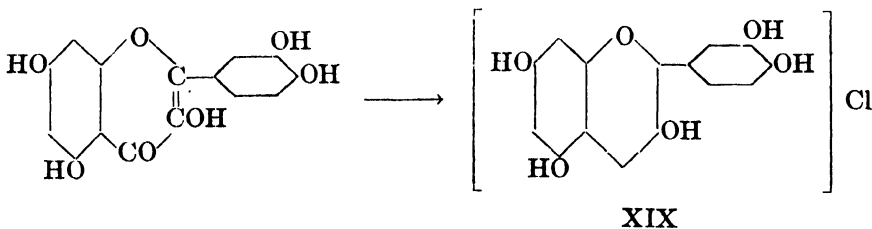
In none of these reactions were benzopyrylium salts isolated, and it was later shown by Heilbron, Hill, and Walls (59) that their production is dependent on the conditions of the experiment and to some extent at least on the nature as well as the position of the substituents. It is necessary to carry out the reaction in dilute solution at room temperature, and under these conditions 3-substituted coumarins are converted smoothly and in good yields into the corresponding 3-substituted flavylium salts. 4-Substituted coumarins under the same conditions give only small quantities of the desired flavylium salts, much of the coumarin being recovered unchanged. Attempts to increase the yield of flavylium salts by employing more concentrated solutions result only in the formation of diaryl- Δ^3 -chromenes without an increase in amount of the monoaryl derivatives. The effect was particularly marked in the cases of 4-methoxy- and 4,7-dimethoxy-coumarins, neither of which could be induced to give a flavyl-



ium salt. Reaction either failed to occur or, under more drastic conditions, resulted solely in the production of substituted Δ^3 -chromenes.

E. The reduction of flavones

In 1914 Everest (39) claimed to have synthesized several anthocyanidins by the reduction of flavones with zinc dust and hydrochloric acid. The experiments were qualitative only and in no instance was the salt isolated, so that the first synthesis of an anthocyanidin must be credited to Willstätter and Mallison (111), who reduced quercetin in methyl alcoholic hydrochloric acid to cyanidin chloride (XIX), using magnesium, zinc dust, or sodium amalgam as the source of hydrogen. The yield was exceedingly small and the product was difficult to isolate.



A similar reduction was reported by Robertson and Robinson (97), who acetylated and reduced rhamnetin by zinc dust in boiling acetic anhydride solution. The product of the reaction was hydrolyzed by alcoholic hydrochloric acid with the formation of rhamnetidin chloride. The yield was again poor and other substances were formed as by-products.

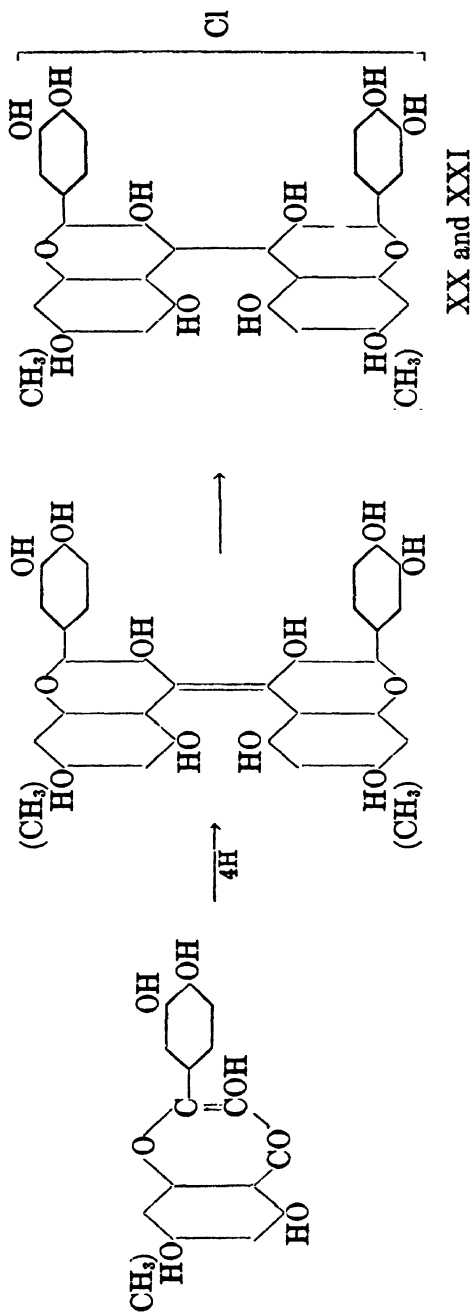
The method has been criticized by Malkin and Nierenstein (79) on the ground that the reduction of other ketonic compounds in acid solution leads to the formation of dimolecular products. They repeated the work of Willstätter and Mallison and of Robertson and Robinson, and claimed that the products described by these authors as flavylum chlorides were, respectively, quercetylene chloride (XX) and 7,7-dimethylquercetylene chloride (XXI), formed according to the scheme on page 38.

No such difference of opinion can hold for the alkaline reductions described by Asahina and Inubuse (3, 4) and Asahina, Nakagome, and Inubuse (5). These authors reduced the flavones apigenin and acacetin, and the flavanones naringenin, sakuranetin, hesperitin, eriodictyol, and homoeriodictyol. The reduction was carried out by suspending the flavone or flavanone in water and treating it with sodium amalgam. After the removal of the mercury the products gave with hydrochloric acid the expected flavylum chlorides, e.g., apigenidin chloride from apigenin, acacetinidin chloride from acacetin etc.

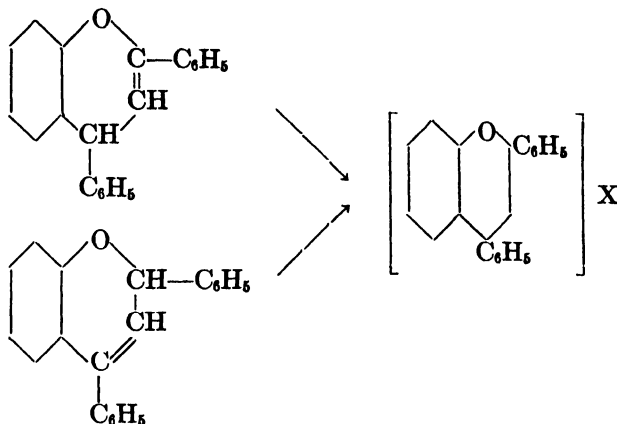
They were unable to reduce quercetin itself by this means, although they succeeded in converting pentamethylquercetin into pentamethylcyanidin chloride. The lack of success with quercetin they attributed to the presence of the free pyrone hydroxyl group. To test this they treated rutin (quercetin rhamnoside with the sugar attached to the pyrone hydroxyl) in the same way and obtained a product which after hydrolysis with boiling hydrochloric acid yielded cyanidin chloride.

F. Oxidation reactions

It will be realized from what has gone before that the successful production of benzopyrylium salts depends on the state of oxidation of the pyrone ring. Similar compounds of a higher state of oxidation (e.g., flavones) may be reduced to the correct state, while in the condensation reactions first described, the reactants are already in the right state of oxidation so that only the elimination of the elements of water is necessary. It is apparent that compounds such as chromans are in a lower state of oxidation than the benzopyrylium salts, and it might be anticipated that a number of syntheses should be reported involving the oxidation of such compounds. The procedure has not been systematically investigated to the same extent as the previously described methods, a number of isolated and apparently unrelated syntheses alone being recorded.



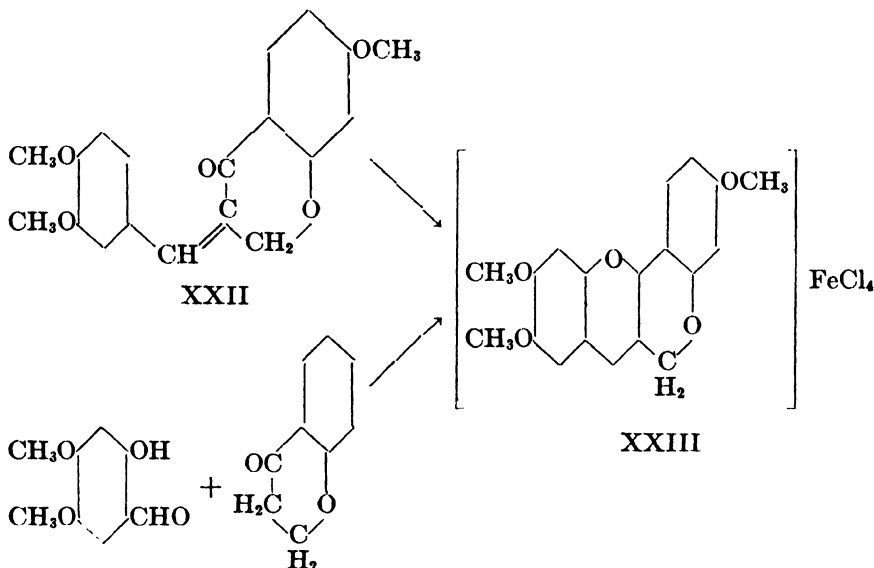
Löwenbein (75) found that the isomeric 2,4-diphenyl- Δ^2 - and Δ^3 -chromenes could be oxidized by ferric chloride (or phosphorus pentachloride or iodine) in acetic anhydride to the same 4-phenylflavylium salt;



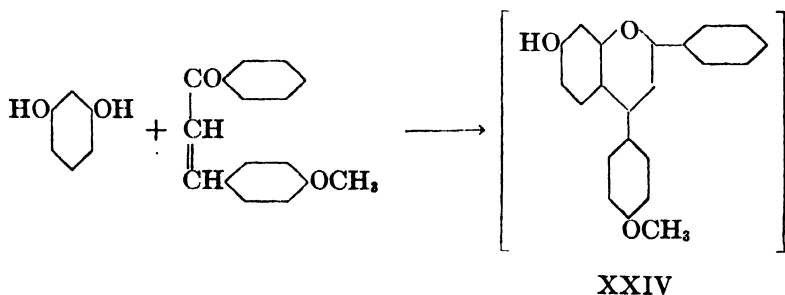
similar oxidations were reported by Löwenbein and Rosenbaum (78). Diltney (33, 34) has used ferric chloride extensively as an oxidation agent for the preparation of substituted pyrylium salts, and Hill (66), using the same reaction with salicylidenediketones, has found that by slight variations in the conditions, either substituted pyrylium salts or flavylium salts resulted. In the same communication Hill also reported the preparation from 4-phenacylflavenes of flavylium salts and 4-phenacylflavylium salts, both of which were formed by oxidation reactions by a mechanism which is still obscure. The anhydro bases of the latter compounds are formed in 50 per cent yield by the action of glacial acetic acid on the diketones, the remainder of the diketone being converted into dihydrochalcone. In this case, therefore, chalcone acts as the oxidizing agent. Two recent reactions which have resulted in the production of pyrylium salts are of interest in this connection. In the preparation of *sym*-trianisylbenzene by the condensation of *p*-methoxyacetophenone under the influence of a mixture of concentrated sulfuric acid and potassium pyrosulfate, Davis and Armstrong (25) found that a part of the product consisted of a 2,4,6-trianisylpyrylium salt. Similarly, Dovey and Robinson (38) found that acetophenone was converted to 2,4,6-triphenylpyrylium borofluoride in the presence of boron trifluoride. In both of these cases there is a loss of a methyl group, although in neither case could methane or its oxidation products be detected.

Another oxidation reaction in which ferric chloride was used as the oxidizing agent was described by Perkin, Ray, and Robinson (86), who found

that 7-methoxy-3-veratrylidenechromanone (XXII) could be oxidized and condensed by ferric chloride in acetic anhydride to form 6,7-dimethoxy-2,3-[7'-methoxychromano-(4',3')]benzopyrylium ferrichloride (XXIII), the constitution of which was later confirmed by its synthesis in the usual manner from 4,5-dimethoxysalicylaldehyde and 7-methoxychromanone (73).

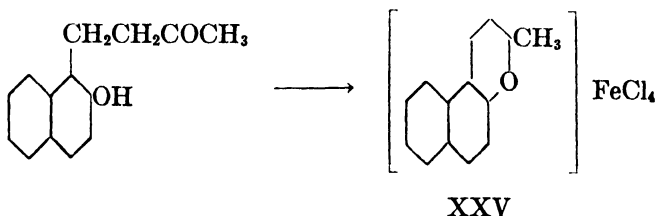


A recent oxidation method which may be regarded as an extension of Bulow's synthesis has been described by Robinson and Walker (102). It involves the condensation of a reactive phenol with an unsaturated aldehyde or ketone in acid solution and in the presence of an oxidizing agent. The particular agent employed was chloranil, and the authors showed that the unsaturated ketone used does not orient itself in both of



the possible ways but gives one product only. Thus, anisylideneacetophenone and resorcinol yielded only 7-hydroxy-4-anisylflavylium chloride (XXIV). In this respect it differs markedly from the Bulow synthesis and should prove a valuable acquisition to the synthetic methods. Its wide applicability was demonstrated by the preparation of many different types of benzopyrylium salts.

Chloranil was also used in conjunction with phosphoryl chloride in an oxidative synthesis described by Miller and Robinson (82). They prepared 2-methyl-5,6-naphtha(1,2)benzopyrylium ferrichloride (XXV) by the ring closure and oxidation of β -(2-hydroxy-1-naphthyl)ethyl methyl ketone followed by conversion into the ferrichloride.



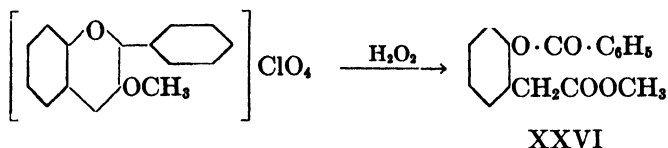
A recent oxidation reaction described by Appel and Robinson (1) converts *d*-catechin, dissolved in technical dioxane, into a bromocyanidin tetramethylether bromide by means of bromine.

The use of phosphorus oxychloride was advocated by Goswami and Chakravarti (51, 52) for the condensation of phenols and coumarins to form benzopyrylium salts, but their results are not conclusive, the compounds obtained not always agreeing with previously described salts of the same constitution.

II. STRUCTURE

A. Introduction

The skeleton of the benzopyrylium salts as used so far in this review has long been regarded as established. Werner (109) and Decker and Fellenberg (29) both postulated the existence of the oxygen heterocyclic ring on the basis of their analytical results, and the synthetic methods employed have supported this view. Conclusive proof of this skeleton was, however, afforded only recently by the oxidation reactions of Dilthey and Quint (94) and Dilthey and Hoeschen (36), who obtained recognizable degradation products from which no part of the original carbon skeleton had been lost. Thus, 3-methoxyflavylium perchlorate was oxidized by hydrogen peroxide in glacial acetic acid to the benzoate of methyl *o*-hydroxyphenylacetate (XXVI).

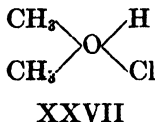


The real interest of the constitution of this group has since rested in the fine structure of the oxygen ring and in the mode of attachment of the acid radical. These two considerations have given rise to much speculation, and a number of different formulas have been proposed for the salts. These fall into three groups depending on whether the anion is regarded as attached to the oxygen (the oxonium theory), to the organic complex as a whole (the centric theories), or to one of the carbons of the oxygen ring (the carbonium and carbenium theories).

B. The oxonium theory

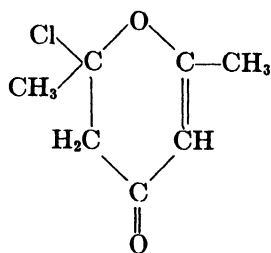
In their first communication on benzopyrylium salts in 1901, Bulow and Wagner (18) considered the compounds to be carbonium salts, but in later papers in the same year they viewed the acid as attached to a quadrivalent oxygen. Werner (109), in the same year, concluded that the xanthylum salts which he had prepared by reducing xanthenes with zinc dust and alcoholic alkali and subsequent treatment of the resulting xanthydrols with acids, were anhydro compounds with the anion attached to the oxygen of the heterocyclic ring.

The possible quadrivalence of oxygen was suggested as early as 1864 by Naquet (83, 84), but it was not until 1875 that Friedel (43, 44) obtained a methyl ether hydrochloride to which the following constitution



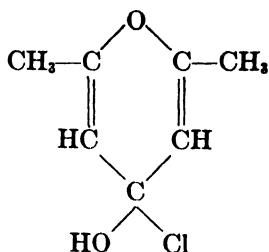
(XXVII) was given. Heyes, in 1888, in order to explain the differences between certain inorganic peroxides, suggested that oxygen might have a valency greater than two (63). In the same year Meldola (81) suggested that the oxygen atom in the azo- β -naphthols might be quadrivalent, and in 1897 Bruhl (13) advocated the quadrivalence of oxygen in hydrogen peroxide. In the meantime compounds of organic substances and acids had been prepared by Baeyer (7), Dale and Schorlemmer (24), Wallach and Gildemeister (107), and Perkin (85). All these authors explained their results on the basis of the accepted valency theory, but in 1899 Collie and Tickle (22) published a paper on the salts of dimethylpyrone and

quadrivalent oxygen, in which they rejected formulas XXVIII and XXIX in favor of a formula (XXX) resembling that for dimethylpyridone



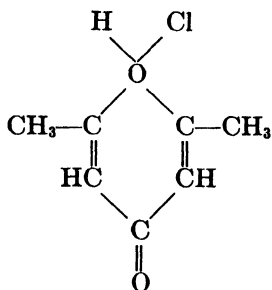
XXVIII

and

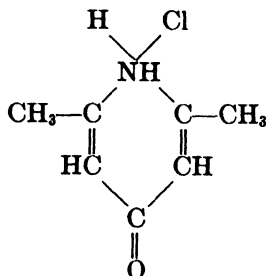


XXIX

hydrochloride (XXXI). Their views were strengthened by the fact that



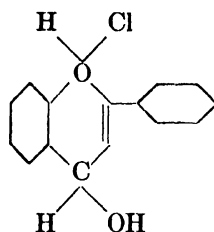
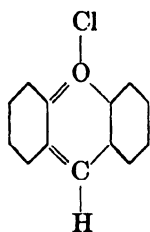
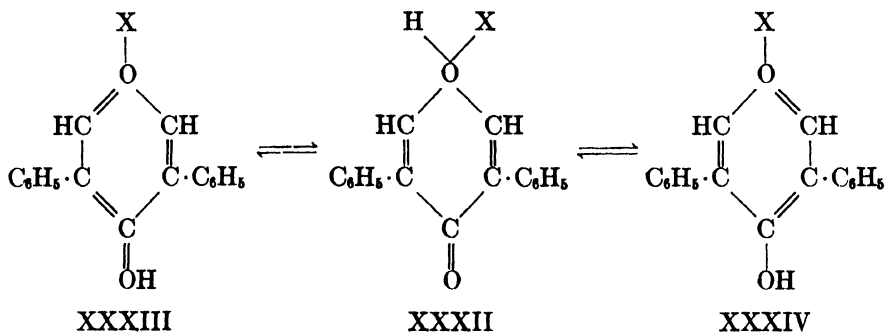
XXX



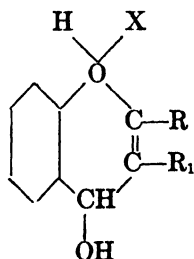
XXXI

the salts were highly colored, and the new formula allowed the adoption of a quinonoid structure in line with the theory of color just then coming into prominence. In their view the third and fourth bonds of the oxygen would be very weak, but according to Baeyer and Villiger this is not necessarily true (9, 10, 11). In the year following Collie and Tickle (22), Hewitt (62) extended their views to account for the fluorescence of some compounds in acid solution and suggested that diphenylpyrone should be represented either by the quinonoidal quadrivalent oxygen compound (XXXII) or by the symmetrical oxonium compounds (XXXIII and XXXIV).

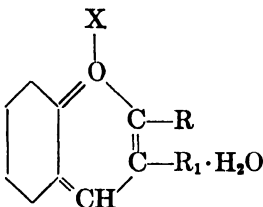
The xanthonium salts of Werner (109) and the benzopyrylium salts of Bulow and Sicherer (16) were therefore represented by formulas XXXV and XXXVI, respectively, and the latter, by simple loss of the elements of water, is readily obtained as the true anhydro oxonium salt corresponding to formula XXXV.



Decker and Fellenberg (28) commenced their investigations on the basis of the oxonium theory, and maintained that the success of their researches was in itself good evidence for the correctness of the theory. As a further point in favor of the oxonium structure they adduced the gradation of stability which they reported finding in the xanthylum, benzopyrylium, and pyrylium salts, which, according to their views based on the series acridine, quinoline, pyridine, was in the expected direction. Their salts were therefore formulated as true oxonium salts. The arguments were expanded in later papers (29, 30, 27), in which they contended that no previous work would explain the basic nature of the compounds without calling in the oxonium theory except the salts of triphenylcarbinol, and these were dismissed from the argument on the ground of the incomparable differences of basicity between the two series.

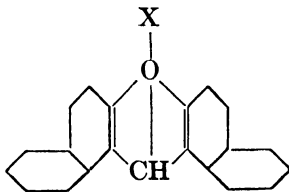


Perkin, Robinson, and Turner (88) retained the quadrivalent oxygen and formulated their salts as pyranol salts of the following constitution, although they were well aware that the water molecule might be present as water of crystallization, in which case the compounds would be, in reality, anhydro salts possessing the oxonium structure.

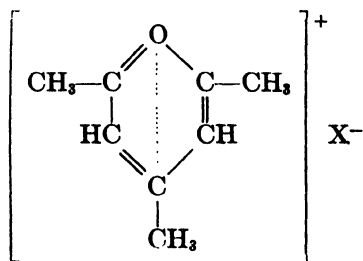


The evidence for or against the anhydro view was not at that time considered conclusive, although the double salts formed with ferric chloride were found to be anhydrous, as Werner had previously found for the xanthylum salts. On the whole, the evidence favored the anhydro formulation and the structure advocated by Decker and Fellenberg was modified, as shown, to include an *o*-quinonoid structure accounting for the deep color of the salts. Willstätter and Mallison (112), who considered both formulas and also a *p*-quinonoid formula, finally adopted the *o*-quinonoid formula of Perkin, Robinson, and Turner, as did also Dilthey (33) for the substituted pyrylium salts.

Fosse (41, 42) utilized the idea of a quadrivalent oxygen in a somewhat different form, and gave the following structure to the dinaphthopyrylium salts which he prepared.



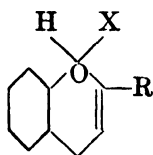
Werner, who first described his xanthylum salts as oxonium compounds (109), later modified his views to a rather similar formula (110) in which the oxygen and the bridge carbon atom were linked by a partial valency with the acid attached in a second sphere; an extension of this has been made by Burawoy (21) to the pyrylium salts by combining the linkage of the oxygen and the 4-carbon atom by a partial valency and uniting the acid radical in an ionized form to the whole positive complex (XXXVII) in the manner developed as described later.



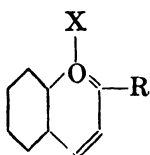
XXXVII

C. The centric theories

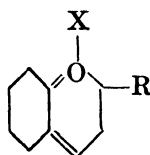
Of the formulas utilizing the quadrivalent oxygen so far described, that of Perkin, Robinson, and Turner (XL) is the most satisfactory.



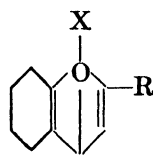
XXXVIII



XXXIX



XL



XLI

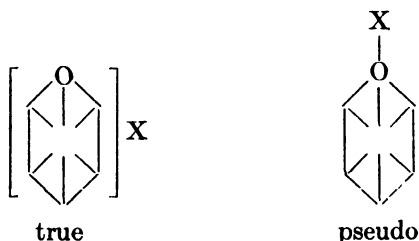
The oxonium theory as a whole, however, possesses certain disadvantages. Although the quadrivalency of oxygen may be defended on the basis of the electronic theory of valency, it cannot be regarded as acceptably proved, and it involves, moreover, the consideration that, contrary to its usual state, the oxygen of the pyrone ring is positively charged. Definite evidence on this point in the actual case of a benzopyrylium salt has been afforded by Le Fevre (74), who nitrated flavylium perchlorate and found the resulting compound to be a *m*-nitro derivative. It follows that the oxygen, which is meta-directing, is in the same state as in benzaldehyde and acetophenone. The consideration of Archibald and McIntosh (2) that the third and fourth valencies are amphoteric, being slightly positive as well as slightly negative, cannot be held to be effective in this case, since the acid medium in which the reaction was carried out would stabilize the salt and oxygen would therefore be, on the oxonium theory, positive.

Oxonium salts were regarded by Collie and Tickle as derivatives of a hypothetical oxonium hydroxide, OH_2OH , and by Decker and Fellenberg of a substituted base $\text{R}_1\text{R}_2\text{R}_3:\text{O}\cdot\text{OH}$, but the pyranols derived from benzopyrylium salts have never been formulated as oxonium compounds and their formation has therefore always presupposed a rearrangement of valencies to permit the hydroxyl group to be attached to either the 2- or

the 4-carbon atom. The fact that Kehrmann and Bohn (71, 72) have found extremely strong bases to exist in the xanthylium series indicates that such a rearrangement does not occur, but that the acid radical and the basic hydroxyl are located in the same place in the molecule, either attached to the oxygen or at some other point.

In more recent years Löwenbein (75), Löwenbein and Rosenbaum (78), and Popper (89) have investigated the action of the Grignard reagent on benzopyrylium salts and have found that there is a simple interchange between the phenyl group of phenylmagnesium bromide and the anion of the salt, with addition of the phenyl group sometimes to the 2- and sometimes to the 4-carbon atom. Such a reaction is difficult to explain by the oxonium theory for, as Löwenbein says "Bemerkenswert ist, dass bei dieser Austauschreaktion die Phenylgruppe den Platz am 4-C-Atom einnimmt, obgleich der Oxonium-Formulierung nach diesem Kohlenstoffatom keine besondere Funktion bei der Salzbildung zukommt."

The difficulties above were evaded, though not explained, by the adoption of the centric formula of Hantzsch (53, 54), in which the anion is placed in a second, ionizable sphere and regarded as attached to the cation complex as a whole. To indicate this the unused valencies are turned inwards, the oxygen still being considered quadrivalent. He distinguished between true and pseudo salts in the pyrylium series and formulated them respectively as follows.

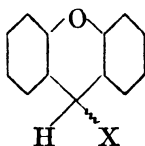


A similar formula was employed by Löwenbein (75).

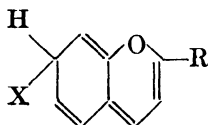
The centric formula forms a link between the oxonium formula and the carbonium and carbenium formulas, since it may be applied to either. Dilthey, for example, favored for a time a type of centric carbonium formula (35) in which the acid radical was attached to the whole cationoid complex. He advanced arguments against the oxonium theory and based his formula upon the work of Kauffmann (70). The acid radical was again supposed to exist in a second sphere, and the unsaturated valencies of the carbon atoms were turned inwards, as in Hantzsch's formula, to indicate that it was not known which of the carbon atoms was involved in the linkage and to facilitate the migration of the hydroxyl of the pseudo base.

D. The carbonium and carbenium theories

It has already been remarked that Bulow and Wagner (18) formulated their salts at first as carbonium compounds. Werner also modified his original views that they were oxonium salts, and Baeyer (8) extended the modification and formulated the xanthylum salts as carbonium compounds (XLII), in which carbon atom 9 and the acid radical were linked by an ionizable valency. Gomberg and Cone (48, 49) and Gomberg and West (50) expressed both the xanthylum and the benzopyrylium salts as "quino-carbonium" compounds (XLIII).

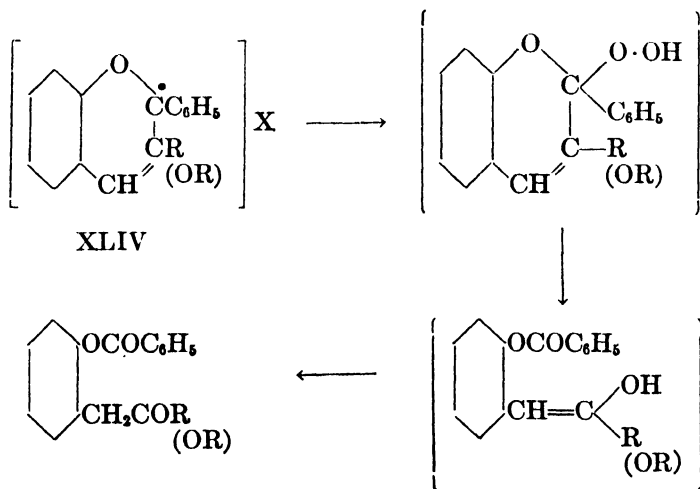


XLII

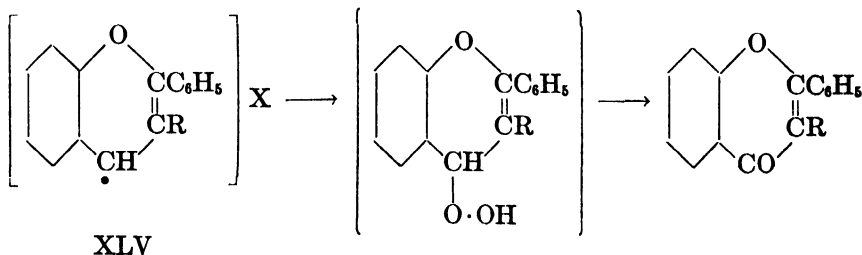


XLIII

The carbonium formula first proposed by Dilthey (35) did not attempt to define the point of attachment of the acid radical, and in an effort to establish this Quint and Dilthey (94) oxidized xanthylum salts by perhydrol in acid or neutral solution. Oxidation commenced at the heteropolar atom with the formation of a peroxide, and by this means they established that in these salts the *meso*-carbon atom was the heteropolar atom. When the same reaction was applied by Dilthey and Quint (37) and Dilthey and Hoeschen (36) to 3-substituted flavylum salts, the peroxide first formed



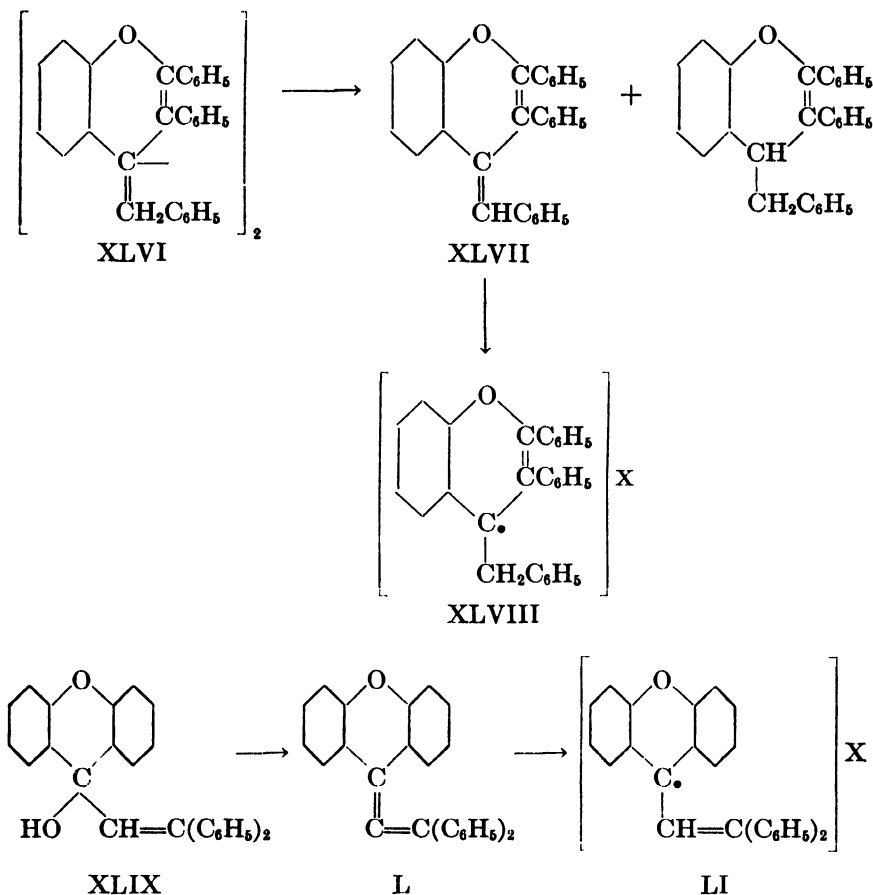
proved to be unstable, and oxidation proceeded further with the formation of benzoyl esters of *o*-hydroxybenzyl ketones (or *o*-hydroxyphenylacetic acid) according to the scheme on page 48, which shows conclusively that the 2-carbon atom is the heteropolar atom and that a double bond occurs in the 3,4-position. Had the 4-carbon atom, for example, been the heteropolar atom, the oxidation must have produced flavones.



On the basis of these results Dilthey and his collaborators introduced a carbenium formula for the benzopyrylium salts. According to this the anion is linked to the pyrone ring at an ionized coördinatively unsaturated carbon atom, the heteropolar atom being indicated by a point as in formulas XLIV and XLV. The complete absence of flavones in their experiments led Dilthey and Hoeschen (36) to conclude that, when localizable, the heteropolar atom in flavylum salts is the 2-carbon atom.

It was suggested by Hill (65), as a result of experiments with salicylidenediacetophenones and 4-phenacylflavenes, that in some instances the 4-carbon atom might also act as a heteropolar atom. This view receives support from many indications in previous work. Thus, the first benzopyrylium salts prepared by Bulow and Wagner (18) were the 2,4-dimethyl derivatives which yielded, instead of the normal pyranols, 2-methyl-4-methyleneflavenes. In the same connection, Löwenbein and Rosenbaum (78) prepared bis-chromenyls containing a benzyl group in the 4-position (XLVI), which readily underwent a disproportionation with the formation of 4-benzylidenefflavenes (XLVII).

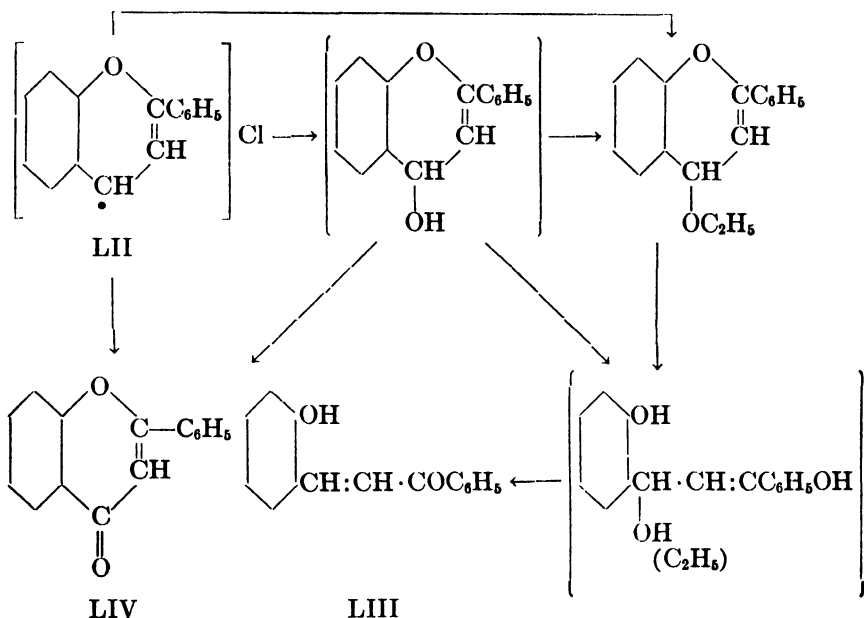
A similar unsaturated compound was described by Ziegler and Ochs (116) by the interaction of xanthone and diphenylvinylmagnesium bromide. The resulting compound was not the expected 9-diphenylvinyl-xanthenol (XLIX), but its dehydration product (L). All these unsaturated compounds spontaneously add acids with the formation of benzopyrylium or xanthylum salts (XLVIII or LI). The reaction between the Grignard compound and benzopyrylium salts whereby addition sometimes occurs at the 2-carbon atom and sometimes at the 4-carbon atom has already been commented upon (75, 78, 89).



There is therefore considerable indirect evidence for assuming that the 4-carbon atom may be the heteropolar atom under conditions which have not so far been investigated. The strongest evidence for this would be the production of flavones. A recent investigation by Hill and Melhuish (67) has established the formation of two distinct types of flavylum salt, which give rise to two series of pyranols, and one of these has been converted into the corresponding flavones. Treatment of 3-substituted flavylum salts with sodium carbonate or sodium hydroxide at room temperature led to the production of pyranols only, but when the same procedure was applied to flavylum salts unsubstituted in position 3, a mixture of products was obtained from which the corresponding chalcones (LIII) and flavones (LIV) were isolated in each case. The explanation of this difference in behavior lies in the properties of the pyranols derived

from the two series of salts. The pyranols derived from flavylum salts unsubstituted in position 3 are unstable and can only be isolated as their ethyl ethers. Even these ethers are comparatively unstable and are converted by simple heating in aqueous alcohol into their respective chalcones. The pyranols from 3-substituted flavylum salts, on the other hand, are stable and can be isolated in the free state. Neither they nor their ethyl ethers are converted into chalcones by aqueous alcohol.

The formation of flavones from salts unsubstituted in position 3 is sufficient evidence that they are flavylum-4-chlorides (LII), and the instability of their pyranols leads to the following scheme of the changes involved.



The salts from which stable pyranols were obtained are those which Diltney and his collaborators have already shown to be flavylum-2-chlorides, and they obviously cannot undergo the reactions outlined above. The fundamental difference exhibited between the two series of pyranols must be reflected in the salts from which they are obtained and this difference is best formulated on the basis of the carbenium theory.

III. REFERENCES

- (1) APPEL AND ROBINSON: J. Chem. Soc. **1935**, 426.
- (2) ARCHIBALD AND McINTOSH: J. Chem. Soc. **85**, 919 (1904).
- (3) ASAHINA AND INUBUSE: Ber. **61**, 1646 (1928).

- (4) ASAHINA AND INURUSE: Ber. **64**, 1256 (1931).
- (5) ASAHINA, NAKAGOME, AND INURUSE: Ber. **62**, 3016 (1929).
- (6) AUWERS: Ber. **45**, 2764 (1912).
- (7) BAEYER: Ann. **183**, 1 (1876).
- (8) BAEYER: Ber. **38**, 574 (1905).
- (9) BAEYER AND VILLIGER: Ber. **34**, 2679 (1901).
- (10) BAEYER AND VILLIGER: Ber. **34**, 3612 (1901).
- (11) BAEYER AND VILLIGER: Ber. **35**, 1201 (1902).
- (12) BLUMSTEIN AND KOSTANECKI: Ber. **33**, 1478 (1900).
- (13) BRUHL: Ber. **30**, 158 (1897).
- (14) BUCK AND HEILBRON: J. Chem. Soc. **123**, 2521 (1923).
- (15) BULOW AND SICHERER: Ber. **34**, 2368 (1901).
- (16) BULOW AND SICHERER: Ber. **34**, 3889 (1901).
- (17) BULOW AND SICHERER: Ber. **34**, 3916 (1901).
- (18) BULOW AND WAGNER: Ber. **34**, 1189 (1901).
- (19) BULOW AND WAGNER: Ber. **34**, 1782 (1901).
- (20) BUNZLY AND DECKER: Ber. **37**, 2931 (1904).
- (21) BURAWOY: Ber. **64**, 462 (1931).
- (22) COLLIE AND TICKLE: J. Chem. Soc. **75**, 710 (1899).
- (23) CORNELSON AND KOSTANECKI: Ber. **29**, 240 (1896).
- (24) DALE AND SCHORLEMMER: Ann. **196**, 75 (1879).
- (25) DAVIS AND ARMSTRONG: J. Am. Chem. Soc. **57**, 1583 (1935).
- (26) DECKER: Chem. Ztg. **30**, 982 (1906).
- (27) DECKER AND BECKER: Ber. **47**, 2288 (1914).
- (28) DECKER AND FELLENBERG: Ber. **40**, 3815 (1907).
- (29) DECKER AND FELLENBERG: Ann. **356**, 281 (1907).
- (30) DECKER AND FELLENBERG: Ann. **364**, 1 (1909).
- (31) DICKINSON AND HEILBRON: J. Chem. Soc. **1927**, 14.
- (32) DICKINSON, HEILBRON, AND O'BRIEN: J. Chem. Soc. **1928**, 2077.
- (33) DILTHEY: J. prakt. Chem. **94**, 53 (1916).
- (34) DILTHEY: J. prakt. Chem. **95**, 107 (1917).
- (35) DILTHEY: Ber. **53**, 261 (1920).
- (36) DILTHEY AND HOESCHEN: J. prakt. Chem. **138**, 42 (1933).
- (37) DILTHEY AND QUINT: J. prakt. Chem. **131**, 1 (1931).
- (38) DOVEY AND ROBINSON: J. Chem. Soc. **1935**, 1389.
- (39) EVEREST: Proc. Roy. Soc. London **87B**, 444 (1914).
- (40) FEUERSTEIN AND KOSTANECKI: Ber. **31**, 710 (1893).
- (41) FOSSE: Bull. soc. chim. [3] **27**, 496 (1902).
- (42) FOSSE: Bull. soc. chim. [4] **5**, 692 (1909).
- (43) FRIEDEL: Bull. soc. chim. [2] **24**, 160 (1875).
- (44) FRIEDEL: Bull. soc. chim. [2] **24**, 241 (1875).
- (45) GHEORGHU AND ARWENTIEW: J. prakt. Chem. **118**, 295 (1928).
- (46) GOLDSCHMIEDT AND KNÖPFER: Monatsh. **18**, 437 (1897).
- (47) GOLDSCHMIEDT AND KNÖPFER: Monatsh. **19**, 406 (1898).
- (48) GOMBERG AND CONE: Ann. **370**, 142 (1909).
- (49) GOMBERG AND CONE: Ann. **376**, 183 (1910).
- (50) GOMBERG AND WEST: J. Am. Chem. Soc. **34**, 1529 (1912).
- (51) GOSWAMI AND CHAKRAVARTI: J. Indian Chem. Soc. **9**, 599 (1932).
- (52) GOSWAMI AND CHAKRAVARTI: J. Indian Chem. Soc. **11**, 713 (1934).
- (53) HANTZSCH: Ber. **52**, 1535 (1919).
- (54) HANTZSCH: Ber. **52**, 1544 (1919).

- (55) HARRIES AND BROMBERGER: Ber. **35**, 3088 (1902).
- (56) HARRIES AND MULLER: Ber. **35**, 966 (1902).
- (57) HEALEY AND ROBINSON: J. Chem. Soc. **1934**, 1625.
- (58) HEILBRON AND HILL: J. Chem. Soc. **1927**, 2005.
- (59) HEILBRON, HILL, AND WALLS: J. Chem. Soc. **1931**, 1701.
- (60) HEILBRON AND IRVING: J. Chem. Soc. **1929**, 936.
- (61) HEILBRON AND ZAKI: J. Chem. Soc. **1926**, 1902.
- (62) HEWITT: Z. physik. Chem. **34**, 1 (1900).
- (63) HEYES: Phil. Mag. [5] **25**, 221 (1888).
- (64) HILL: J. Chem. Soc. **1934**, 1255.
- (65) HILL: J. Chem. Soc. **1935**, 85.
- (66) HILL AND MELHUISE: J. Chem. Soc. **1935**, 88.
- (67) HILL AND MELHUISE: J. Chem. Soc. **1935**, 1161.
- (68) HOUBEN: Ber. **37**, 489 (1924).
- (69) IRVINE AND ROBINSON: J. Chem. Soc. **1927**, 2086.
- (70) KAUFFMANN: Ber. **52**, 1422 (1919).
- (71) KEHRMANN AND BOHN: Ber. **47**, 82 (1914).
- (72) KEHRMANN AND BOHN: Ber. **47**, 3052 (1914).
- (73) KELLER AND ROBINSON: J. Chem. Soc. **1933**, 1533.
- (74) LE FEVRE: J. Chem. Soc. **1929**, 2771.
- (75) LÖWENBEIN: Ber. **57**, 1517 (1924).
- (76) LÖWENBEIN AND KATZ: Ber. **59**, 1377 (1926).
- (77) LÖWENBEIN AND ROSENBAUM: Ann. **448**, 223 (1926).
- (78) LOVETT AND ROBERTS: J. Chem. Soc. **1928**, 1975.
- (79) MALKIN AND NIERENSTEIN: J. Am. Chem. Soc. **52**, 2864 (1930).
- (80) MALKIN AND ROBINSON: J. Chem. Soc. **127**, 1190 (1925).
- (81) MELDOLA: Phil. Mag. [5] **26**, 403 (1888).
- (82) MILLER AND ROBINSON: J. Chem. Soc. **1933**, 1535.
- (83) NAQUET: Compt. rend. **58**, 381 (1864).
- (84) NAQUET: Compt. rend. **58**, 675 (1864).
- (85) PERKIN: J. Chem. Soc. **69**, 1439 (1896).
- (86) PERKIN, RAY, AND ROBINSON: J. Chem. Soc. **1926**, 950.
- (87) PERKIN AND ROBINSON: Proc. Chem. Soc. **19**, 149 (1907).
- (88) PERKIN, ROBINSON, AND TURNER: J. Chem. Soc. **93**, 1085 (1908).
- (89) POPPER: Dissertation, University of Berlin, 1925.
- (90) PRATT AND ROBINSON: J. Chem. Soc. **121**, 1577 (1922).
- (91) PRATT AND ROBINSON: J. Chem. Soc. **123**, 739 (1923).
- (92) PRATT AND ROBINSON: J. Chem. Soc. **127**, 166 (1925).
- (93) PRATT AND ROBINSON: J. Chem. Soc. **127**, 1182 (1925).
- (94) QUINT AND DILTHEY: Ber. **64**, 2082 (1931).
- (95) RIDGEWAY AND ROBINSON: J. Chem. Soc. **125**, 214 (1924).
- (96) ROBERTSON AND ROBINSON: J. Chem. Soc. **1927**, 1710.
- (97) ROBERTSON AND ROBINSON: J. Chem. Soc. **1927**, 2196.
- (98) ROBINSON: Chemistry and Industry **1933**, 737.
- (99) ROBINSON: Ber. **67A**, 85 (1934).
- (100) ROBINSON: Nature **135**, 732 (1935).
- (101) ROBINSON AND LAWSON: J. Chem. Soc. **125**, 213 (1924).
- (102) ROBINSON AND WALKER: J. Chem. Soc. **1934**, 1435.
- (103) ROBINSON AND WALKER: J. Chem. Soc. **1935**, 941.
- (104) RUHEMANN AND LEVY: J. Chem. Soc. **103**, 551 (1913).
- (105) RUPE AND VEIT: Chem. Zentr. **1906**, I, 1417.

- (106) STOERMER AND WEHLN: Ber. **35**, 3549 (1902).
- (107) WALLACH AND GILDEMEISTER: Ann. **246**, 265 (1888).
- (108) WEIDEL AND WENZEL: Monatsh. **21**, 62 (1900).
- (109) WERNER: Ber. **34**, 3300 (1901).
- (110) WERNER: Ann. **322**, 296 (1902).
- (111) WILLSTÄTTER AND MALLISON: Sitzber. preuss. Akad. Wiss. **34**, 769 (1914).
- (112) WILLSTÄTTER AND MALLISON: Ann. **408**, 15 (1915).
- (113) WILLSTÄTTER AND SCHMIDT: Ber. **57**, 1945 (1924).
- (114) WILLSTÄTTER AND ZECHMEISTER: Sitzber. preuss. Akad. Wiss. **34**, 886 (1914).
- (115) WILLSTÄTTER, ZECHMEISTER, AND KINDLER: Ber. **57**, 1938 (1924).
- (116) ZIEGLER AND OCHS: Ber. **55**, 2257 (1922).

A SYMPOSIUM ON COMPLEX INORGANIC COMPOUNDS¹

INTRODUCTION TO THE SYMPOSIUM

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No apology need be made for a more extended study and discussion of the subject of complex inorganic compounds. In fact, it would be difficult to define such an all-inclusive term as "complex compound," for the simple reason that the formation of complexes is an inherent feature of many chemical reactions. The assumption is prevalent among many chemists that the compounds so designated are the well-known cobalt, chromium, and platinum ammines first studied in detail by Werner and his students. It should be evident from the titles listed for discussion at this symposium that the Werner complexes represent only a special division of an exceedingly diverse and extended class of substances.

Actually there is little difference, except one of degree, between the well-known Werner complexes of cobalt, chromium, and platinum, and many other ammines (ammonates), hydrates, and the great number of organic and inorganic molecular addition compounds. It makes little difference whether the coördinating atom is metallic or non-metallic in character, or whether the coördinated constituent is an atom, ion, or molecule. The same sort of bonding characterizes ammines, hydrates, and other solvates. It is also the distinguishing characteristic of the linkages in the iso- and hetero-poly acids, and the amphoteric oxides, amides, sulfides, and cyanides. The covalent link accounts for the formation of many complex minerals. The argon-boron trifluoride compounds recently discovered by Booth and his coworkers owe their existence to the fact that the argon atom may donate a pair of electrons to boron.

Recent developments in theoretical chemistry and in research technique have given new prominence to this field. The Brönsted concept of acid-base equilibria has directed attention to complex ions in the development of acidic and basic properties in solution, while the ever-changing theories

¹ Presented before the Division of Physical and Inorganic Chemistry at the Ninety-first Meeting of the American Chemical Society at Kansas City, April 16, 1936.

of atomic structure have demanded investigation of the physical and chemical properties of compounds characterized by the covalent link. The modern interest in theories of optical activity has stimulated careful investigation of the optical properties of both organic and inorganic substances. At the same time, improved apparatus and the development of new research techniques, such as are furnished by x-ray and electron diffraction methods, have made it possible to gain new knowledge of the structure of all types of compounds.

From a purely practical point of view there is every reason for a more detailed study of complex inorganic compounds. We need think only of the applications and the uses of complex compounds in analytical chemistry in the qualitative detection and quantitative estimation of many cations and anions, and as indicators. Complex cyanides are formed in the separation of precious metals from their ores and are used in the electrodeposition of many metals. The organic chemist has long used various poly acids for the precipitation of certain alkaloids. Attention has also been directed to the use of complex compounds as specific reagents for the isolation of certain amino acids.

The opportunities for investigational work in this field seem to be unlimited. The formation of complex, or "solvated" ions should most certainly be considered in any theory of electrolytic solution which is proposed. Unfortunately, chemical interaction of solvent with solute is tacitly disregarded in most of our modern theories. The number of complex compounds which have been studied by x-ray methods is relatively small. This valuable tool of research should be pressed into service for the determination of the structures of many more of these substances. It should be pointed out that altogether too little is known concerning the stability relationships among complex compounds. A general theory of amphoterism as applied to amphoteric oxides, amides, sulfides, cyanides, etc., is in need of elucidation. Formation of large molecular aggregates or complexes in a further study of colloidal behavior would seem important. Methods of preparation of many of the complex inorganic compounds are largely empirical. Here the synthetic inorganic chemist has a field of endeavor which should warrant his utmost efforts. As a tool for research complex compounds offer innumerable possibilities in the study of configuration, isomerism, and the mechanism of optical activity.

In considering papers for presentation at this symposium the chairman suffered from an embarrassment of riches. The subjects chosen for discussion indicate the varied character of the investigational possibilities in the field of complex inorganic compounds. It is to be hoped that subsequent symposia will give opportunity for discussion of other phases of this extremely interesting subject.

To Professor Rodebush (and W. M. Latimer) must be given the credit for first pointing out the possibility of coördination through the hydrogen bond. In his paper on the hydrogen bond and coördination Professor Rodebush cites many examples of hydrogen bonding in accounting for such interesting phenomena as association of molecules in the liquid state and anion solvation. A new theory for the behavior of the unusual solutions of the alkali and alkaline earth metals in liquid ammonia is also presented.

Professor Bailar has been singularly successful in applying the methods of the organic chemist to the study of isomeric relationships among the cobalt complexes. The Walden inversion, so common in organic chemistry, finds its counterpart in the case of the optically active inorganic complexes. The possibility of employing optically active Werner complexes in the resolution of organic compounds is also an interesting feature of the paper by Professor Bailar.

Recent concepts of solvolysis and solvation, and the behavior of complex ions as acids and bases are reviewed by Professor Hall. The earlier experimental findings of Werner, Lamb, and others are interpreted in terms of our modern theories. It is significant in this connection that much of Werner's work on his own oxonium theory fits in very nicely with our present views.

The polyhalides have always puzzled the theoretical chemist. Their relationship to certain parent solvents is discussed by Professor Booth,² who has greatly extended this class of compounds by preparing a whole series of polyhalides containing fluorine.

² The fifth paper in this symposium, entitled "The Polyhalides" and presented by Harold Simmons Booth of Western Reserve University, was received too late for publication in this issue, but will appear in a subsequent number.—Editor.

THE HYDROGEN BOND AND COÖRDINATION

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The concept of the hydrogen bond was developed by W. M. Latimer and the author in 1920 (7) to account for the behavior of associated solvents. The article which was published at that time grew out of a discussion concerning some work that had been done upon the dielectric constant of liquid ammonia at the University of Kansas under the direction of H. P. Cady some years earlier.¹ At that time there was a great deal of confusion in regard to the use of the term "polar." While the measurement of dipole moments was not then the common practice that it became a few years later, it was, of course, recognized that the molecules of both water and hydrogen chloride had moments in the gaseous state. These two substances behave very differently in the liquid state. The peculiar properties of water as a solvent were ascribed to association through the formation of hydrogen bonds. Not only was the hydrogen bond assumed to account for the action of the solvent on the ionization of acids and bases, but it was assumed that the high dielectric constant, and hence the solvent power of these peculiar solvents for electrolytes in general, was due to hydrogen-bond formation.²

It was not until nearly fifteen years later that the experimental proof

¹ The author undertook the measurement of the dielectric constant of liquid ammonia in 1913. This work was subsequently finished by W. M. Latimer. The results were never published, but the data obtained were in substantial agreement with results which are now in the literature.

² It has often been assumed that another type of association would account for the low dielectric constant of hydrogen chloride in the condensed state, but it seems more probable that there is no association at all in this case. Hildebrand (5) has directed attention to the small energy involved in dipole interaction. Pauling (10) predicted that hydrogen chloride molecules would rotate in the crystal near the melting point and show a high dielectric constant. While Pauling's prediction is undoubtedly correct, the dielectric constant is not very great. In the gaseous state only those molecules which are in the zero rotational state contribute to the dielectric constant. While one would not be justified in considering the liquid simply as a condensed gas, one may suspect that the relatively low dielectric constant is accounted for in part, at least, by the presence of freely rotating unassociated molecules.

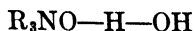
of the existence of this bond was obtained. The x-ray studies of Zachariasen (14) and of Pauling upon crystals, and the electron diffraction studies of Pauling (11) upon organic molecules have shown that it is a common occurrence for oxygen, nitrogen, or fluorine atoms to be linked together by a hydrogen atom. More recently Wulf (4) and his collaborators have discovered that the bond in the neighborhood of 1.5μ is not shown in absorption when the hydrogen is doubly linked. This bond is the first harmonic of the vibration of a hydrogen atom linked to oxygen or nitrogen. We thus have not only a test, but a quantitative measure of the amount of hydrogen bonding present in a substance.

Formally the hydrogen bond may be regarded as a case of coördination of the simplest cation, the proton. The coördination number of a cation decreases with the ratio of the cation-anion radii; the limiting value of the coördination number for zero radius is two. The hydrogen ion from a strong acid in solution may, therefore, coördinate two molecules of the solvent just as the cupric ion may coördinate four molecules of ammonia. For example, the hydrate $\text{HCl}(\text{H}_2\text{O})_2$ is well known. Of course, one of the coördinated molecules may be the anion of the acid itself, as in $(\text{C}_2\text{H}_5)_2\text{OHCl}$ and other oxonium compounds. If the acid is weak the anion of the acid is always coördinated, and if the acid is very weak, then there is no ionization, and no hydrogen bond is formed, as, for example, when hydrogen is linked to aliphatic carbon. The limitation to a certain range of acid strengths limits the hydrogen bond to the atoms of nitrogen, oxygen, and fluorine, although there is some evidence of weak bonding with other halogens. The energy of dissociation of a hydrogen bond probably never exceeds 6 to 7 large calories. It is, therefore, rather less than the bond energy of a typical coördination bond, as, for example, the $\text{Ag}^+ - \text{NH}_3$ linkage, and for this reason molecular complexes involving hydrogen bonds have not received the attention in the past that has been given to the well-known class of complexes which were studied so extensively by Werner.³

As examples of hydrogen bonding, we may mention such widely different complexes as pyridine dihydrochloride and the amine oxide dihydrates. The amine oxides are an interesting group of compounds which are very soluble in water and form very stable hydrates. It was at first predicted that the amine oxides would be strong bases as are the quaternary am-

³ Efforts to formulate a quantum mechanical description of the hydrogen bond have not been particularly successful, for the obvious reason that the bonding energy is small and a very exact calculation would be required to ascertain even the sign of the energy. Sherman, Huggins, and Bernal have discussed this problem. The latter has introduced the concept of a "hydroxyl" bond, but it is not clear that he is talking about anything different from the hydrogen bond.

monium compounds, but when the possible electronic structures were considered it was seen that they could not be bases at all, except through hydrogen-bond formation.



As a matter of fact, they are weak bases, as would be predicted.

One of the most important rôles of the hydrogen bond is in the association of solvent molecules. Presumably all cases of typical "association" in solvents involve hydrogen-bond formation. Both water and ice are highly associated in this way. One of the most interesting results of such association is the tendency of the alcohols to form glasses on supercooling. This tendency has been shown by Zachariasen (15) to be due to hydrogen bonding in the case of methyl alcohol. A glass is likely to be formed when a molecule has the possibility of coördinating a small number, four or less, of its neighbors through definite linkages, whereas the geometry of the situation permits a larger number. Under these conditions, there is opportunity for the disorientation characteristic of a glass.

By far the most interesting of the associated solvents is hydrogen fluoride, and it is here that the strongest hydrogen bond is formed. The remarkable work of Fredenhagen (2) probably needs to be confirmed in some particulars by other investigators, but it furnishes us with conclusions. It will be more logical, however, to consider this substance in connection with anion solvation and to continue the discussion of its behavior under that topic in the latter part of this paper.

The hydration of the lyophilic substances found in living tissue, such as the carbohydrates and proteins, must be in a large part due to the hydrogen bond. There are no cations of the heavy metals present to account for hydration by the Werner type of coördination, and no ions at all in many cases. The problem of bound water, which has been regarded in the past as a colloidal phenomenon, seems likely to resolve itself into a chemical problem. The term "colloidal," like the term "catalytic," is often used to cover chemical ignorance.

As a matter of fact, there is evidence to confirm this idea. In 1911, Coblenz observed that the infra-red absorption band at 1.5μ was missing in gelatin, which presumably contained a good deal of water, thus anticipating the discovery of Wulf by twenty-five years. Buswell (1), in 1929, noted the fact and suggested that the hydrogen bond might be involved in the binding of water by gelatin.

It has been assumed by some that any water in a salt hydrate which is not coördinated with the cation through the Werner type of bonding must be associated with the anion. The recent work of Hendricks (3) and collaborators on the ammonium oxalate crystal indicates that this is not

necessarily so; the water in the crystal may simply be filling holes. However, no one would doubt the existence of anion solvation. It is usually due to the formation of the hydrogen bond, and because this bond is relatively weak, it is more difficult to determine the extent of solvation of the anion.

The anion has not only a negative electron atmosphere in its periphery, but a negative over-all charge, so that hydrogen bonding is favored, whereas in the cation the net positive charge must repel the hydrogen strongly.

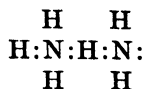
Just as the simplest proton is the cation, so the simplest anion is the electron, and we have a beautiful example of solvation of the electron in the extremely interesting solutions of the alkali metals in liquid ammonia. While the existence of these solutions has been known for a long time, it is due to the work of that great trio of investigators, Franklin, Cady, and Kraus, who began their researches in this field at the University of Kansas, that we understand their nature as well as we do. The brilliant and daring hypothesis that the electron in these solutions is solvated is due to Kraus (6). But many chemists have wondered how it is possible for an ammonia molecule which, in the light of our present knowledge of electronic structure can have no electron affinity, to attract and hold an electron.

Before we attempt to answer this question, we will do well to ask ourselves: Why does sodium dissolve in liquid ammonia in the first place? Every possible sort of guess has been made by speculators upon this subject, and some of them were undoubtedly upon the right track. It is only necessary for us to select the plausible hypotheses.

We may note that sodium alloys with mercury and other liquid metals, but that it does not dissolve in any non-metallic solvent except ammonia and the amines. It may be argued, of course, that sodium dissolves in the more polar solvents, but that it reacts with them so rapidly that the solution cannot be observed. This argument cannot be disproved, but we may suspect that sodium will form solutions only with metals, and that the clue to the solubility of sodium in liquid ammonia lies in the possibility of the formation of metallic ammonium. This is, of course, not a new idea.

Let us recapitulate briefly the properties of dilute solutions of sodium in ammonia. The equivalent conductivity approaches a limiting value greater than 1000 reciprocal ohms. The sodium moves toward the cathode and the transference ratio as determined from E.M.F. measurements indicates that the sodium has the normal equivalent conductivity of the sodium ion (about 130 ohms⁻¹). If a little water be added to the solution, however, a violent reaction characteristic of sodium metal is obtained. The sodium plays a dual rôle as metal and as ion at one and the same time.

The whole behavior can be understood if we assume that the sodium atom is in resonance, so to speak, with an NH_4 radical, so that the electron passes readily back and forth between the two. There are no ammonium ions in solution, but ammonia molecules associated in groups of two or more through hydrogen bonds forming complexes such as



The tendency of the NH_4 ion to acquire an electron and behave as a metal is well known. It is stable until two such groups come together, when the reaction



takes place. In the absence of ions, especially of the amide ion, there is no tendency for two NH_4 groups to come together and the hydrogen-forming reaction does not take place. There is also little or no tendency for the ammonium complex to dissociate according to the reaction



In dilute solution, the sodium exists in the form of ions and the electron is associated with the ammonium. When conducting, the electron jumps from one ammonium group to another. This is essentially metallic conduction.⁴

The more concentrated the solution, the greater the mobility of the electron. If the electron were firmly attached to any group, no such mobility would be possible, but the ionizing potential of the ammonium group must be small.⁵ The high mobility of the electron is, therefore, analogous to the high mobility of the hydrogen ion in water solutions. The acquirement of the electron by the ammonium radical must be accompanied by a large increase in volume, which accounts for the surprising increase in volume of sodium in liquid ammonia. The sodium and ammonium are solvated in the solution, but the most important thing is the formation of complexes containing NH_4 groups through hydrogen-bond formation.

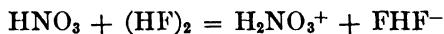
⁴ The sodium ion probably forms a complex of the type $\text{Na}(\text{NH}_3)_n^+$, and it might be assumed that this is the group with which the electron is associated. In dilute solution, however, where the dissociation is complete, the electron must be associated with the ammonia. Triethylamine cannot form hydrogen bonds, and has a very low dielectric constant. It should not form metallic solutions of the alkali metals if the above considerations are correct.

⁵ The work of Leighton (9) and colleagues seems to indicate that the photoelectric threshold for the ammonium ion itself is not much less than that of the alkali metals.

Let us return to hydrogen fluoride, already mentioned as a case of anion solvation. Apparently the strongest hydrogen bonds that occur are formed with fluorine, and Simons (13) has shown that the vapor of hydrogen fluoride tends to form benzene-like polymers $(\text{HF})_n$, linked through hydrogen bonds. The single molecule HF is a weak acid, for reasons which have been pointed out elsewhere. On the other hand, $\text{H}(\text{FHF})$ must, for similar reasons, be a strong acid.

The F^- tends to associate HF to form the FHF^- ion just as it tends to hydrate, and the hydrogen bond formed here must be very strong. But there is very little tendency for two HF molecules to associate in water solution. With a high concentration of HF molecules, as in liquid hydrogen fluoride, there must be a great deal of this type of association, but now there can be no ionization, because acids only ionize in basic solvents.

On the other hand, if nitric acid is dissolved in the hydrogen fluoride, the molecule is solvated through hydrogen-bond formation (as it is in water), but this process is accompanied by ionization of the hydrogen fluoride, according to the reaction



Hence, as seems reasonable, hydrogen fluoride behaves as the strongest known acid when in high concentrations.

Anion solvation is an important factor in determining the solubility of salts. The actual solubility of a salt is a complex function of charge, radius, and coördination power (12). The coördination power may depend upon charge, the possibility of forming hydrogen bonds, and van der Waals' forces. The latter, for example, are very important in the case of silver iodide, where both ions contain a large number of electrons. It must not be forgotten that a cation may coördinate its own anion. The calculation of solubility is, therefore, very difficult, although Fajans has attempted to give some semiquantitative rules. There are cases, however, where the solvation of the anion plays a predominant rôle. The nitrate ion, for example, is a large ion of single charge with a strong tendency to hydration, and it is not surprising, therefore, that nitrates are soluble.

There is reason to think that deuterium forms stronger hydrogen bonds than does hydrogen (8). The investigation of deuterium compounds promises to be of great interest.

REFERENCES

- (1) BUSWELL, A. M.: American Chemical Society Monograph, No. 38, p. 53. The Chemical Catalog Co., Inc., New York (1928).
- (2) FREDENHAGEN, K., AND CADENBACH, G.: Z. physik. Chem. **146A**, 245 (1930).
- (3) HENDRICKS, S. B., AND JEFFERSON, M. A.: J. Chem. Physics **4**, 102 (1936).

- (4) HILBERT, G. E., WULF, O. R., HENDRICKS, S. B., AND LIDDELL, U.: J. Am. Chem. Soc. **58**, 548 (1936).
- (5) HILDEBRAND, J. H.: Science **83**, 21 (1936).
- (6) KRAUS, C. A.: J. Am. Chem. Soc. **43**, 749 (1921).
- (7) LATIMER, W. M., AND RODEBUSH, W. H.: J. Am. Chem. Soc. **42**, 1419 (1920).
- (8) LEWIS, G. N., AND SCHUTZ, P. W.: J. Am. Chem. Soc. **56**, 493 (1934).
- (9) OGG, R. A., JR., LEIGHTON, P. A., AND BERGSTROM, F. W.: J. Am. Chem. Soc. **55**, 1754 (1933).
- (10) PAULING, L.: Phys. Rev. **36**, 430 (1930).
- (11) PAULING, L., AND BROCKWAY, L. O.: Proc. Nat. Acad. Sci. **20**, 336 (1934).
- (12) RODEBUSH, W. H.: Trans. Faraday Soc. **30**, 778 (1934); see also FAJANS, K.: Z. angew. Chem. **43**, 1046 (1930).
- (13) SIMONS, J., AND HILDEBRAND, J. H.: J. Am. Chem. Soc. **46**, 2183 (1924).
- (14) ZACHARIASEN, W. H.: J. Chem. Physics **1**, 634 (1933).
- (15) ZACHARIASEN, W. H.: J. Chem. Physics **3**, 162 (1935).

THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

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The stereochemistry of carbon has been investigated so extensively that stereochemistry is commonly considered as a chapter in the study of organic compounds. This thought was so firmly fixed in the minds of the preceding generation that many chemists felt that Werner's resolutions of metal ammines into optical antipodes depended upon the fact that he used organic amines (such as ethylenediamine) as coördinating groups. Werner's postulate that the hexammine metal ion is octahedral was universally accepted only after he had resolved an ion containing no carbon.

More recently, x-ray investigations, electron-diffraction studies, dipole-moment measurements, and other physicochemical methods have greatly extended our knowledge of the spatial relationships of the atoms of inorganic, as well as organic, compounds. The important principles of stereochemistry, however, are still those which were discovered through the study of organic compounds, and which, in some cases, have been shown to be applicable to other elements having four tetrahedral valences. But the tetravalent elements are not necessarily tetrahedral, and it is quite probable that some of them are planar, at least in certain types of compounds. The hexavalent elements are evidently octahedral, and present several times as many possibilities for isomerism and intramolecular rearrangement as do the compounds of carbon. Very little is known about the stereochemistry of elements having coördination numbers greater than six, but the relationships must be extremely complex.

The complexity of the stereochemistry of inorganic compounds makes it difficult to establish generalizations and to formulate theories on the basis of observations of these compounds. On the other hand, we have here an extremely useful tool for testing the theories of the organic stereochemist. A theory may describe the behavior of a tetrahedral molecule very well, but if it cannot predict behavior in molecules of other structures, it is in error in some particular. Moreover, when working with the complex inorganic compounds, it is possible to achieve conditions which cannot be achieved with the carbon compounds. Thus, it is possible to com-

pare the stereochemical properties of analogous compounds of different elements; it is possible to vary the valence of the central atom of the complex; and it is possible to achieve optical activity when the center of asymmetry is attached to two or more identical univalent groups.

No attempt is made in this paper to discuss the stereochemistry of the complex inorganic compounds completely. A few of the more important problems which have been reported are described here in the hope of stimulating interest in this investigational field.

TETRACOVALENT METALS

The question of the spatial distribution of the valences of the tetravalent elements has received a great deal of attention and has inspired an enormous amount of research. It is well known that the valences of carbon, nitrogen, sulfur, and many other tetravalent elements are arranged tetrahedrally, and there seems to be no substantial evidence that the valences of the elements named are ever otherwise. Among certain of the tetravalent metals, the case is not nearly so simple, since there is evidence for the existence of both tetrahedral and planar structures for several of them. It is still an open question whether the experimental work has been incorrectly interpreted or whether some elements can assume more than one structure.

The fact that dichlorodiammineplatinum exists in two forms led Werner (88) to propose a planar arrangement of the four valences of the platinum atom. His interpretation was unchallenged until 1926, when Reihlen and Nestle (73) carried out molecular weight determinations of the two forms (cryoscopically in liquid ammonia) and found one of them to be dimolecular. Werner's fundamental postulate was upheld, however, by Hantzsch's (28) discovery that both forms of $[\text{Pt}(\text{py})_2\text{Cl}_2]$ (py = pyridine) are monomolecular in phenol and by Grünberg's demonstration (25) of the monomolecular structure of both forms of $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$. Dozens of pairs of such isomers have been studied. There seems little reason to doubt that planar structures exist for several of the metallic elements, though some of the cases reported have been found to be in error.¹

The supposition of planar structures for the tetravalent platinum, palladium, and nickelous ions is supported by several x-ray studies. Dickinson (16) has shown the anions of K_2PtCl_4 and K_2PdCl_4 to be planar, and Cox (10) has reported that the four nitrogens of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ are in the same plane as the platinum atom. X-ray investigations of many other compounds of nickel, palladium, and platinum have confirmed these discoveries (11).

¹ For example, Drew, Pinkard, Preston, and Wardlaw (20) have shown that the pallado-diammines exist in only one series, and that the supposed isomeric series (40) is actually polymeric.

The discovery of three isomers of $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})(\text{C}_6\text{H}_5\text{N})(\text{NO}_2)]\text{NO}_2$ (84) further confirms the planar arrangement of the valences of the platinous ion. Incidentally this is the only compound of tetravalent platinum known in which four different groups are coordinated to the platinum atom.

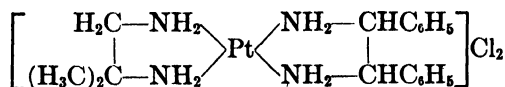
Still further support for the planar structure of these complexes of platinum, palladium, and nickel is deduced from the existence of isomeric forms of chelated spiran compounds of the type



The tetrahedral structure postulates mirror-image isomers; the planar structure postulates *cis-trans* isomers, differing in physical and chemical properties, but having no optical activity. Actually, several cases of such geometric isomerism are known. Dwyer and Mellor have obtained isomeric forms of bisantibenzylmethylglyoximeplatinous chloride (23) and the corresponding palladium salt (24) differing in color, melting point, solubility, and stability. To see whether these compounds have a planar or pyramidal structure, Dwyer and Mellor attempted to resolve them—one of them would be optically active if the molecule is pyramidal—but were unable to prepare salts of optically active acids.

Other examples of unsymmetrical chelate compounds which have been obtained in *cis* and *trans* forms are to be found in the work of Grünberg and Ptizyn (27), Pinkard, Sharratt, Wardlaw, and Cox (65), Sugden (83), Drew and Head (18) and many others.

Mills and Quibell (61) have recently demonstrated in a most ingenious way that the valences of platinous platinum are not tetrahedral. They prepared *meso*-stilbenediaminoisobutylenediaminoplatinous chloride

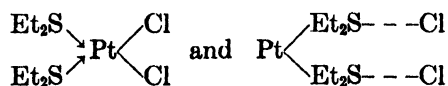


by the successive action of isobutylene diamine and *meso*-stilbenediamine on potassium chloroplatinite. If the valences of the platinum be in a plane, this compound will have no plane of symmetry and must be optically active. If, on the other hand, the valences of the platinum form a regular tetrahedron, the molecule will possess a plane of symmetry. Actually, the compound was resolved into isomers of high optical stability. On the basis of atomic radii considerations, Mills and Quibell have deduced that for this compound, the planar arrangement actually produces less strain in the molecule than does the tetrahedral.

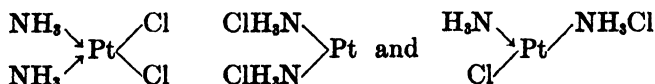
Jensen (35) has recently determined the dipole moments of several compounds of the type $\text{PtX}_2(\text{SR}_2)_2$, where X represents Cl, Br, I, NO_2 , or NO_3 , and R represents ethyl, propyl, isopropyl, butyl, isobutyl, secondary-butyl, or benzyl. The α (*trans*)-compounds give values of about 2.4×10^{-18} e.s.u., the β (*cis*)-compounds containing halogen values of 9×10^{-18} e.s.u., and the β -compounds containing nitrite and nitrate values of 13×10^{-18} e.s.u. While these results are in accord with Werner's configuration determinations, it is significant that the α -compounds do not have zero moment. The moment of 2.4×10^{-18} e.s.u. may be reconciled with the planar arrangement by assuming that the valence angles of the sulfur atom are tetrahedral and that the R groups all lie on one side of the plane. However, it is difficult to understand how this unsymmetrical structure would be maintained.

Finally, it should be pointed out that Pauling (64) has shown on strictly theoretical grounds that divalent nickel, palladium, and platinum should have planar structures. His views have been given partial confirmation by the work of Sugden (83), who has studied the isomeric forms of nickel benzylmethylglyoxime. It should be emphasized that the foregoing statements refer only to the metals in the divalent state. Brockway and Cross (9) have pointed out that Pauling's calculations indicate a tetrahedral structure for neutral nickel and they have shown, by electron-diffraction studies, that nickel carbonyl is probably tetrahedral. Cox and Webster (13) have made an x-ray study of trimethylplatonic chloride, $(\text{CH}_3)_3\text{PtCl}$, in which the platinum is tetravalent and quadrivalent. The molecule is not planar, and is presumably tetrahedral.

The recent work of Drew and his associates deserves some mention, for it strikes at the theory of planar distribution of the bonds, and indeed at the coordination theory itself. Angell, Drew, and Wardlaw (1) have examined the isomeric forms of $\text{Pt}\{(\text{C}_2\text{H}_5)_2\text{S}\}_2\text{Cl}_2$ and concluded that they are structural isomerides with formulas



Drew, Pinkard, Wardlaw, and Cox (21) have reported the discovery of a third isomer of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and have ascribed the formulas



to these compounds. Their work has been criticized by Rosenblatt and Schleede (76), and their interpretation by Bassett (6) and by Jensen (36).

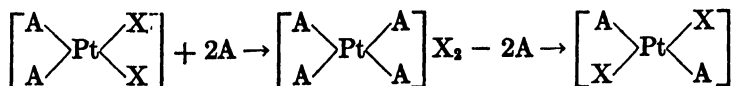
Lifschitz and Froentjes (48) believe they have found support for Drew's formulas, but Jensen (37) feels that their results are fully explained on the basis of Werner's formulas. If the formulas proposed are correct, the assumption of planar configuration for the platinum atom has no support. Drew and his coworkers have therefore abandoned it, and have proposed a new theory to account for the reactions of the isomers (17, 19, 22). They suppose that the four valences are grouped in two pairs, the members of each pair being more closely related to each other than they are to those of the other pair. These rather revolutionary proposals cannot be accepted until they have been substantiated by further work.

Several methods have been devised for distinguishing between the *cis* and *trans* isomers. The well-known method of Werner (89), while lacking a theoretical basis, has proven very useful. Grünberg (26) has postulated that a divalent group can occupy two coordination positions only if those positions are *cis* to each other, and that if this group be displaced by two univalent groups, they will occupy the same positions. Thus α -[Pt(NH₃)₂Cl₂] and [Pt(NH₃)₂(C₂O₄)] can readily be converted into each other. The β -[Pt(NH₃)₂Cl₂], however, yields an acid oxalate [Pt(NH₃)₂(C₂O₄H)]¹ when treated with oxalic acid. The α -form is therefore the *cis* isomer and the β -form the *trans* isomer. Glycine, ethylenediamine, and other groups which normally occupy two coordination positions can be used in place of oxalic acid.

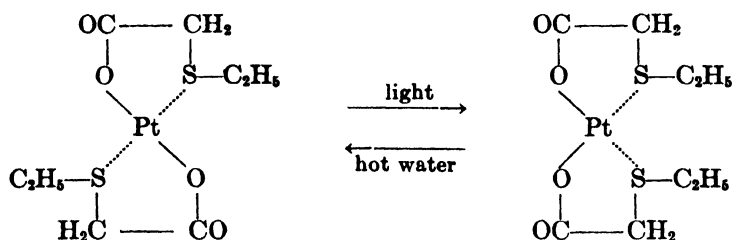
Kurnakow (42) has reported that many platinous salts of the type [PtA₂X₂] (A is ammonia or an amine, and X is a negative ion) react with thiourea, the *cis* salts giving compounds of the type [Pt{CS(NH₂)₂}]₄X₂ and the *trans* giving [Pt{CS(NH₂)₂}]₂(NH₃)₂X₂.

The two types of salts can often be distinguished by differences in properties. The *cis* salts are usually darker in color, more soluble, and have lower melting points.

In some cases the *cis* form changes to the *trans* form very readily. In other cases continued heating is required to effect the change. Thus *cis*-di(triethylphosphine)dichloroplatinum changes to the *trans* form upon heating to 100°C. in a sealed tube with alcohol. In accordance with Werner's principle of "trans elimination" the *cis* forms of the type PtA₂X₂ can be changed to *trans* by adding and removing two molecules of the amine

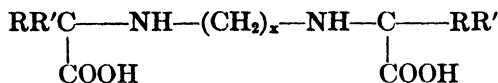


Ramberg (67) has observed that the *cis* and *trans* isomers of platinous ethyl thio glycolate can be readily interconverted.

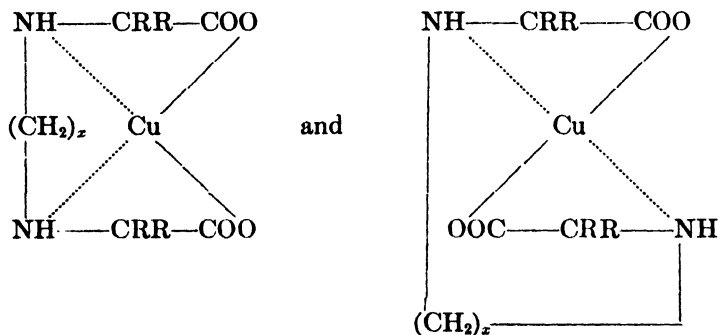


This work has been criticized by Reihlen and Nestle (74), who hold that the platinum is tetrahedral, and that the existence of two forms is due to the presence of the two asymmetric sulfur atoms.

N. Schlesinger (79) has prepared salts of copper with *bis*(α -imino) acids of the type



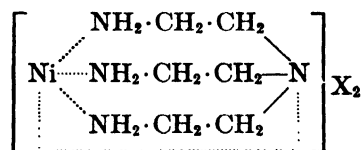
Acids containing two or three methylene groups give water-soluble, blue compounds, those containing ten give insoluble violet compounds, and those containing five or seven give mixtures of the two types. Schlesinger explained these as *cis-trans* isomers.



Obviously the "*cis*" is the blue form, and the "*trans*" the violet form. Reihlen (69), however, has called attention to the fact that, since nitrogen is tetrahedral, the copper either is not planar in these compounds or is subject to great strain. He explains the existence of isomers in the following way: If the $-\text{CH}_2-$ groups lie "inside" the two nitrogen atoms, a bridge of two or three can span the distance between the nitrogen atoms. If the hydrogen atoms lie "inside" the nitrogens and the $-\text{CH}_2-$ groups "outside," a bridge of at least seven methylene groups is required.

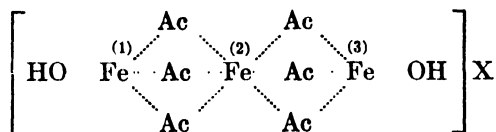
Cox and his coworkers (12, 15) have recently carried out x-ray studies on several complex compounds of bivalent copper, and have found that the four coordinated groups lie in the same plane with the copper.

It is firmly established that the valences of some of the tetravalent elements are non-planar. Compounds of carbon, sulfur, boron, and many other elements exist in optically active forms, which precludes the possibility of a planar arrangement. Even those elements which have been shown to have a planar arrangement must be able also to assume a non-planar configuration. The nickel, platinum, and palladium β , β' , β'' -triaminotriethylamine salts of Mann and Pope (53) are almost certainly non-planar. The nickel compound has been shown to be monomeric; consequently it probably has the structure (70)



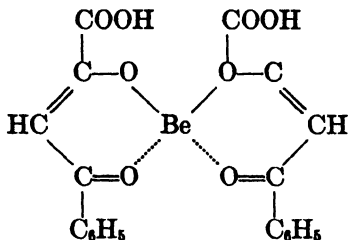
Cox and Webster (14), in reporting the results of x-ray studies on these nickel salts, have pointed out that there is no evidence to show that they are not "pseudo salts" containing hexavalent nickel.

Reihlen (68) pointed out long ago that Werner's formulas for basic ferric and chromic acetates



indicate a three-dimensional configuration. Each of the triplets of acetate groups fills the three corners of a face of the central octahedron. Metal atoms 1 and 3 are therefore centers of three-dimensional figures or are parts of the face of the octahedron, which seems unlikely.

The tetrahedral configuration implies asymmetry and optical activity for certain types of compounds. A considerable amount of work has been done on the resolution of inorganic complex compounds of tetravalent elements. Lowry and Burgess (49) observed that the beryllium salt of benzoylcampbor mutarotates in certain organic solvents. Mills and Gotts (60) prepared beryllium, zinc, and copper compounds of benzoylpyruvic acid:



The beryllium compound was resolved through the brucine salt, and the brucine was precipitated by dimethylaniline. The material so obtained racemized in a few minutes. The brucine salt of the zinc compound and the strychnine salt of the copper compound were shown to mutarotate.

Apparently the first attempt to resolve compounds of tetravalent platinum was made by Rosenheim and Händler (78). The compounds which they studied were too unstable to give positive results. Reihlen and his coworkers had somewhat better success. Reihlen and Hühn (71) resolved the *bis*-(1,2-isobutylenediamine)-platinous and -palladous ions and the *bis*-(2-aminomethyl-3-methyl-4-ethylquinoline)-platinous, -palladous, and -nickel ions through the α -bromocamphor- π -sulfonates. They prepared α -phenylethylenediamine-(2-aminomethyl-3-methyl-4-ethylquinoline)platinous salts (72) and were able to fractionate the α -bromocamphor- π -sulfonate. Reihlen, Seipel, and Weinbrenner (75) prepared and resolved *l*- α -phenylethylenediaminedipyridylplatinous salts and other similar salts. Rosenheim and Gerb (77) resolved the *bis*(2,3-diaminotoluene)-platinous and -palladous ions. In no case, however, have the nickel, platinous, or palladous salts been obtained in optically active form after the removal of the resolving agent. The results are, therefore, not entirely certain.

Hein and Regler (30) have recently reported that crystallization of *bis*-(8-hydroxyquinoline)argentate α -bromocamphor- π -sulfonate yields fractions of different rotatory power.

Hantzsch and Rosenblatt (29) have suggested that the tetrammine platinum compounds are not true salts of the type $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, but are octahedral "pseudo salts" $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$ in which the platinum is hexavalent. In ionizing solvents, the chlorine atoms are expelled from the complex, as chloride ions, by the entrance of solvent molecules. Evidence for the existence of such pseudo salts is found in the abnormally low conductivity of $\text{Pt}(\text{pyridine})_4(\text{SCN})_2$ and similar salts in alcohol, and in the fact that several of these salts show different absorption spectra in solvents which form solvates than in those which do not. It should be mentioned in this connection that divalent platinum is undoubtedly hexavalent in

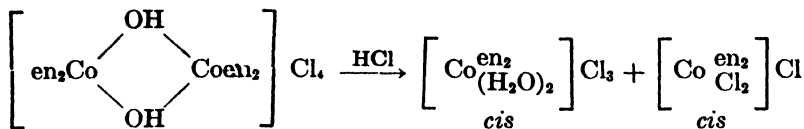
some compounds. By assuming the octahedral structure for the tetramine, the theory accounts for both geometric and optical isomerism.

HEXACOVALENT METALS

The stereochemistry of the hexacovalent metals is remarkably complex and very little has been done to unravel the problems it presents. This is largely due, no doubt, to experimental difficulties. Methods of synthesizing even the simple compounds are quite empirical, and it is as yet impossible to build very complex molecules of known configuration. Even if it were possible to synthesize the desired compounds, the problem of determination of configuration would still have to be met. The complexity of the problem is evident from the fact that a molecule in which six different groups are coordinated to the central atom should exist (assuming the octahedral theory) in thirty different configurations,—fifteen pairs of mirror-image isomers. The elementary state of our knowledge of the problem can be seen from the following considerations: The two simplest cases in which isomerism are possible are those in which (1) two coordinated groups are alike, but different from the other four, and (2) two groups are unlike and different from the other four. It is possible to synthesize many compounds of each type and in most cases to tell which is *cis* and which is *trans*. For the closely related compounds of the types $[MA_2b_2]$ and $[MA_2bc]$ (A represents a group occupying two coordination positions) it is also possible to distinguish between the *cis* and the *trans*, and in some cases to resolve the *cis* forms into optical antipodes. Resolution is likewise possible for compounds of the type $[MA_3]$. Beyond these simplest types, our knowledge is very slight. Compounds of other types have been described, but in most cases their configurations are not known.

Several methods are available for determining the configurations of the compound of the types $[Ma_4b_2]$ and $[MA_2b_2]$. Isomerism in these cases is apparently impossible when a group occupying two coordination positions is substituted for the groups b. Werner assumed (91) that the compound formed in such case has the *cis* configuration, and that if the doubly bound group be replaced by two singly bound groups (b) these will be *cis* to each other. For example, carbonate tetrammine cobaltic salts react with hydrochloric acid to give purple dichloro salts. These must be *cis*. The green isomeric dichloro salts, therefore, have the *trans* configuration. If we substitute other bases for ammonia, or other halogens for chlorine, the green and purple colors persist, and indicate the configurations of these compounds.

The doubly bridged dinuclear complexes can also be used for determinations of configuration. These are assumed to be joined in the *cis* positions, and when broken, *cis* compounds are formed.



(In these formulas "en" represents ethylenediamine.)

Cis compounds of certain types are resolvable into optical antipodes, but *trans* compounds are not. This furnishes an absolute method of determining configurations for molecules of the types $[\text{MA}_2\text{b}_2]$ and $[\text{MA}_2\text{bc}]$.

The *cis* compounds are usually but not always more soluble, less stable, and more intensely colored than the *trans* compounds. The *cis* compounds also have a greater electric moment than the *trans*.

In many cases it is possible to change a *cis* compound to the *trans*, or *vice versa*. Thus, *cis*-dinitrodiethylenediaminocobaltic nitrite changes to the *trans* isomer when its water solution is boiled for a long time. *Trans*-dichlorodiethylenediaminocobaltic chloride changes to the *cis* form on heating in water. The presence of acid, however, causes the reverse change to take place. Reactions in which coordinated groups are displaced often lead to changes in configuration. Werner (91) made an extended study of this phenomenon, but as yet we know very little about it. A few of Werner's results are presented in table 1.

No general rules can be drawn from these results. Reactions 1 and 2, 6 and 7, 8 and 9, and 12 and 13 show that the configuration of the product has no relationship to the configuration of the original material. The last pair mentioned is the most striking, for change of configuration takes place in both reactions. This case has been subjected to a detailed study (7). Several bases were used to carry out the reaction, and the conditions of temperature and concentration were varied over a wide range, but the result in every case was the same as Werner reported. In some cases, however, the conditions of the experiment affect the relative amounts of the two isomeric products very markedly.

To explain these results Werner assumed (90) that the incoming group is subjected to the attractive force of the central ion, and that this attractive force is exerted in a definite direction which determines what position the group shall occupy. The group which is least firmly bound is expelled, and there is no connection between the positions of the incoming and outgoing groups. This problem is certainly in need of further study.

The complex inorganic compounds lend themselves well to the study of optical rotatory power. Many of them are simple in structure, have absorption bands in the visible region, and have very high rotatory powers. Studies of the rotatory power of these compounds have been made by Jaeger² (32), Lifschitz (45), Johnson (38, 39), and others, and many in-

² For a summary of his results see reference 32.

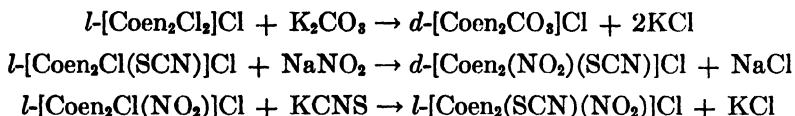
TABLE 1
Results obtained by Werner in a study of changes in configuration

REACTION	STARTING MATERIAL		REAGENT	PRODUCT	RATIO OF	
	cis	trans			cis	trans
1		+	Liquid NH ₃	[Coen ₂ (NH ₃) ₂]Br ₂	20	1
2	+		Liquid NH ₃	[Coen ₂ (NH ₃) ₂]Br ₂	6	1
3		+	Liquid NH ₃	[Coen ₂ (NH ₃)(SCN)Cl(SCN)]Br ₂	2	1
4		+	Liquid NH ₃	[Coen ₂ (NH ₃)(SCN)]Br ₂	1	2
5		+	Liquid NH ₃	[Coen ₂ (NH ₃)(SCN)](ClO ₄)Br	2	1
6		+	KSCN	[Coen ₂ (SCN) ₂]SCN		*
7		+	KSCN	[Coen ₂ (SCN) ₂]SCN	**	*
8	+		AgOH	[Coen ₂ (NH ₃)(OH)]X ₂		*
9		+	AgOH	[Coen ₂ (SCN)(OH)]X ₂	*	*
10		+	NH ₄ OH	[Coen ₂ (SCN)(OH)]Cl		*
11	+		KSCN	[Coen ₂ (SCN) ₂]SCN	*	
12		+	KOH	[Coen ₂ (H ₂ O)(OH)]X ₂		*
13	+		Concd. NH ₄ OH	[Coen ₂ (H ₂ O)(OH)]X ₂		*

* = chiefly; ** = quantitatively.

teresting facts have been brought to light. Johnson has deduced from atomic structure considerations that not all compounds of the type $[MA_3]$ are resolvable. The trioxalato salts of cobalt and chromium which are held together by "electron bonds" have been resolved, but those of manganese and iron have not, and, according to Johnson, are incapable of resolution, since they are held together by "ionic bonds."

In an effort to find a relationship between configuration and direction of rotation, Werner (92) carried out many transformations involving optically active compounds:



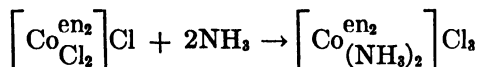
He assumed that no change in configuration took place during these reactions, and formulated structures in accord with this assumption. The results of resolution of some of the compounds mentioned gives some evidence for this view. $[\text{Coen}_2\text{Cl}(\text{SCN})]\text{Cl}$, $[\text{Coen}_2\text{Cl}(\text{NO}_2)]\text{Cl}$, and $[\text{Coen}_2(\text{NO}_2)(\text{SCN})]\text{Cl}$ were resolved through fractionation of the *d*- α -bromocamphor- π -sulfonates. Werner assumed that the complex ions of the same configuration form in each case the less soluble salt with the active acid. The results obtained agree with those derived from the first assumption, for the *l*- $[\text{Coen}_2\text{Cl}(\text{SCN})]^+$, *d*- $[\text{Coen}_2\text{Cl}(\text{NO}_2)]^+$, and *d*- $[\text{Coen}_2(\text{NO}_2)(\text{SCN})]^+$ ions crystallized with the bromocamphorsulfonate in the first fractions. Werner has applied these principles to other cases as well. Jaeger (33) has criticized these views, and has sought to relate configuration to sign of rotation by a study of the crystal forms of the compounds in question. From studies of the optical absorption and rotation of many optically active complex salts, Mathieu (54) has found some support for Werner's rule relating configuration and solubility of the diastereoisomers.

Several methods of correlating configuration with sign of rotation have been suggested recently. Werner Kuhn (41) has deduced absolute configurations of both organic and inorganic compounds from the theory of the origin of optical rotation. Mathieu (55) has suggested that the study of circular dichroism leads to a determination of configuration. Tsuchida, Kobayashi, and Nakamura (86) have reported that when finely-powdered quartz is shaken with solutions of certain racemic complex compounds, it preferentially adsorbs one antipode, compounds of the same configuration being preferentially adsorbed by quartz of a given sign of rotation. The method may also be used to determine whether a given compound is "*cis*" or "*trans*". Thus, when a solution of chloroamminobisdimethylglyoxime cobalt is shaken with the quartz powder, the supernatant liquid

is optically active (87). The complex compound must therefore have the *cis* configuration.

Werner's assumption that atoms or groups in the complex ion are always displaced by others without change of configuration is certainly wrong, for it has been shown (2) that silver carbonate reacts with *l*-dichlorodiethylenediaminocobaltic chloride to give *l*-carbonatodiethylenediamino salts, while potassium carbonate gives the dextrorotatory product. A more recent study (4) has shown that an excess of silver carbonate gives the levorotatory product, while a deficiency gives the dextrorotatory salt. It is interesting to consider this result in the light of the suggestions of Bancroft and Davis (5). From a study of the reaction of bases with halo-succinic acids, they have concluded that the degree of inversion is a function of the acidity of the solution. Such an explanation may not hold in this case, for silver carbonate, like potassium carbonate, is basic. However, the greater the quantity of silver carbonate employed, the higher the negative rotation of the product, while potassium carbonate always gives a dextrorotatory product.

Inversion occurs also when ammonia reacts with dichlorodiethylenediaminocobaltic chloride to form the diammino salt (3):



At the boiling point of liquid ammonia, and at lower temperatures, the product has the same sign of rotation as the original material (0.1 per cent solutions, D line for the dichloro salt and E line for the diammine), but at room temperature or higher, the sign of rotation is reversed. A little of the *trans* salts is always formed, the amount varying with the conditions of the experiment, but it is not yet known what factors control this change.

The fact that inversion can take place in this reaction is very interesting, for it throws some light upon a recent theory of the Walden inversion. Olson (63) and Polanyi (8, 56) have suggested (on the basis of the reactions of organic molecules) that inversion accompanies *every* reaction. If the reaction takes place in one step, the initial and final products have opposite configurations; if it takes place in two steps, inversion takes place twice, and the product has the same configuration as the original salt, etc. In this case two chlorine ions, occupying identical positions in the molecule, are displaced by ammonia molecules. It seems logical to suppose that the same mechanism functions in displacing the two ions. There must, then, be an even number of steps in the complete process, and according to the theory, inversion could not take place. (Formation of the *trans* salts could take place through the steps *cis* → *cis* → *trans* and race-

mization through the steps *cis* \rightarrow *trans* \rightarrow *cis*). If the two chlorine atoms are not displaced in the same way, inversion may take place.

Meisenheimer's theory of the Walden inversion (57, 59) postulates that the incoming group attaches itself to the face of the tetrahedron opposite the group to be expelled. For the octahedral model, there is no face opposite a corner, but there are four "opposite" faces all equidistant from each corner. If we consider that the incoming group may attach itself to any one of these four faces, the theory of Meisenheimer will predict complete racemization, as a study of the model will show.

If optically active groups are introduced into molecules of the type $[MA_3]$ some remarkably interesting properties appear. Jaeger and Blumendal (34) have worked with *trans*-1,2-cyclopentylenediamine (cyc). For the complex ion consisting of three molecules of this base and a metal ion, eight stereoisomeric forms are theoretically possible,—*Dddd*, *Dlll*, *Dddl*, *Ddll*, *Lddd*, *Llll*, *Lddl*, *Ldll* (*D* and *L* represent the configurations of the complex ion and *d* and *l* the configurations of the base). For the cobalt and rhodium complexes Jaeger and Blumendal obtained only two compounds,—*Dlll* and *Lddd*. The asymmetry of the base has induced asymmetry in the complex, so that we have a partially asymmetric synthesis.

When racemic $\left[Co \begin{smallmatrix} en_2 \\ Cl_2 \end{smallmatrix}\right]Cl$ was treated with racemic cyclopentylenediamine, $\left[Co \begin{smallmatrix} en_2 \\ cyc \end{smallmatrix}\right]Cl_3$ was formed. Resolution gave only two of the four possible isomers,—*Dl* and *Ld*. When the levo form of the base was used, however, both of the possible isomers were formed,—*Dl* and *Ll*.

Jaeger and Blumendal also prepared the compound $\left[Co \begin{smallmatrix} cyc_2 \\ Cl_2 \end{smallmatrix}\right]Cl$, using the racemic base. Of the three theoretically possible isomers of the *trans* configuration (*dd*, *ll*, *dl*), only two seemed to form,—*dd* and *ll*. These, on being heated in water, gave the corresponding *cis* forms. For both the *cis* and the *trans* forms, the rotation of the complex was opposite to that of the free base. Attempts were made to introduce the levo base into the complex containing the dextro base, and *vice versa*, but the expected compounds, if formed at all, decomposed to a mixture of the more symmetrical types. The same effect was observed when ethylenediamine was introduced into the molecule:



Evidently the desired compounds were formed in this case, but were too unstable to be separated from the solution.

In building up complexes containing 1,2-propylenediamine (pn) still another complexity is introduced, for in addition to being optically active,

propylenediamine is unsymmetrical. Smirnoff (82, see also 85) prepared the platonic and cobaltic tripropylenediamino salts, and observed that it is not possible to have both the levo and dextro base in the same complex ion. Here again the rotation of the complex is opposite that of the base. Smirnoff did not detect any isomerism due to the unsymmetrical nature of the propylenediamine molecule.

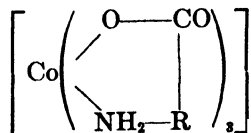
These results hint that a molecule of the type $\left[M \begin{smallmatrix} l_2 \\ x_2 \end{smallmatrix} \right]$ (where l is a levo-rotatory base such as cyclopentylenediamine or propylenediamine and x is a univalent group) might react more readily with another molecule of the levo base than with a molecule of the dextro base. If this is the case, a molecule of the complex, treated with an excess of the racemic base, might react with the levo component, leaving the dextro component uncombined, and thus effect a resolution of the base. Several attempts to produce such an effect have been made in the author's laboratory,³ but positive results have not yet been achieved.

Werner and Smirnoff (96) investigated the case of *cis*-ethylenediamino active propylenediamino-dinitrocobaltic salts. The complex may be either *D* or *L*, the propylenediamine may be either *d* or *l*, and for the *cis* form the methyl group of the propylenediamine molecule may be either adjacent to the plane containing the nitro groups or distant from it. If all of the possibilities are realized, eight isomers will exist. Werner and Smirnoff succeeded in obtaining all of them, thus confirming the predictions of the octahedral theory in a most brilliant manner. The two *trans* salts were also isolated.

Hürlimann (31) investigated the active dipropylenediaminocobaltic salts. Of the great number of isomers possible, only four seem to form,—namely, two pairs of optical antipodes. In one of the pairs the propylenediamine molecules have the same configuration; in the other, they are of opposite configuration. No isomerism due to the position of the methyl group could be detected. None of the six possible *trans* salts was found.

These phenomena have no counterpart in the stereochemistry of carbon. It is quite possible that further study in this field would yield results of great value to stereochemistry.

Ley and his coworkers (43, 44) have studied some amino acid chelate compounds of the type

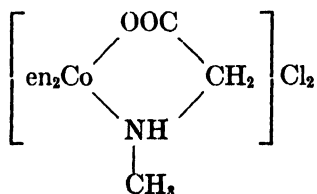


³ This work has been done by Dr. J. H. Balthis, Mr. C. A. Stiegman, and Mr. E. H. Huffman.

Each of the glycine, alanine, and picolinic compounds exists in two forms (one violet and one red) in one of which the nitrogen atoms are all *cis* to each other (1:2:3), while in the other two nitrogen atoms are *trans* to each other (1:2:6). No method of distinguishing between them has been developed. Both the violet and the red forms are asymmetric, but cannot be resolved as they do not form salts. Chelated amino acid salts of platinum and chromium were also prepared. Using *d*-alanine, Lifschitz (46) obtained three forms of the cobalt salt,—two violet and one red. The two violet forms are supposed to be diastereoisomers, *Dddd* and *Lddd*. If this explanation is correct, there should be two red forms also. Lifschitz did not isolate them, but he obtained evidence for their existence.

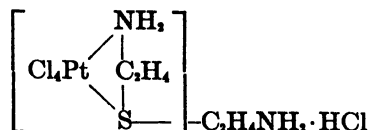
Shibata and his colleagues (80, 81) studied the catalytic oxidation of certain racemic amino acids in the presence of optically active complex compounds and reported that one isomer of the amino acid is oxidized faster than the other. They attribute this to an "enzyme-like action" of the inorganic complex. An alternative explanation would be that one form of the amino acid becomes part of the complex, while the other does not. Subsequent oxidation might destroy one or the other. Pugh's results (66) are not entirely in accord with those of Shibata.

In a metal ammine, each nitrogen atom may be considered the center of a "secondary" complex. This was strikingly illustrated by Meisenheimer, Angermann, Holsten, and Kinderlen (58), in demonstrating the tetrahedral nature of the nitrogen atom. Sarcosine-diethylenediaminocobaltic chloride



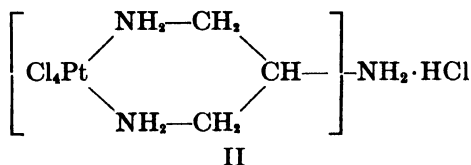
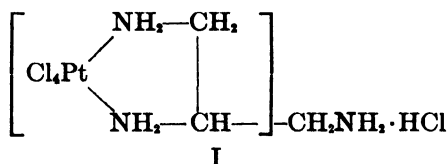
was converted to the bromocamphorsulfonate, which upon crystallization yielded two forms, evidently $(\text{Co} - \text{N}\pm)$ and $(\text{Co} + \text{N}\pm)$. The second, upon recrystallization from water, gave a salt with a molecular rotation (for the D line) of $+2290^\circ$. This gradually decreased to $+2020^\circ$, which is the value for the $(\text{Co} + \text{N}\pm)$ form. Two of the other three isomers were obtained in the impure state. Their rotations changed in solution to that of the nitrogen racemic compound.

The same principle is illustrated in the resolution of $(\beta, \beta'$ -diaminodiethyl sulfide monohydrochloride)tetrachloroplatinum,

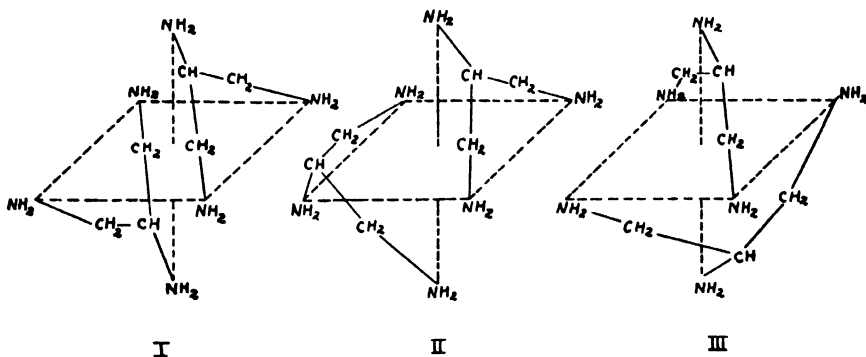


which was accomplished by Mann (51). In this case the sulfur atom is asymmetric.

A somewhat different case involves the resolution of (α , β , γ -triaminopropane hydrochloride)tetrachloroplatinum, which was also reported by Mann (50). The platinum and nitrogen atoms are not asymmetric, so that optical activity must be due to a carbon atom, which has become asymmetric in the formation of the complex. Coordination evidently takes place through the α and β groups (structure I) rather than through the α and γ groups (II).



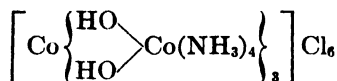
It is possible for a single group to occupy three or even four coordination positions. Mann and Pope (52) prepared cobalt and rhodium salts of α , β , γ -triaminopropane, in which each molecule of the base occupies three coordination positions. Such a salt should exist in three forms, two of which (II and III) are asymmetric.



Only one isomer was obtained; evidently it is much more stable than the others, and is formed preferentially. There was some evidence of optical activity, but the results in this regard are not definite.

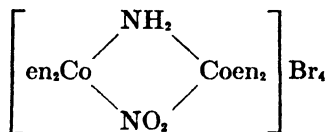
Morgan and Main-Smith (62) demonstrated that ethylenediaminobisacetylacetone (abbreviated "ec") acting in the enol form, $\text{CH}_3 \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{C}(\text{OH}) \cdot \text{CH}_3$, can occupy four coordination positions. All five of the possible stereoisomers of the compound $[\text{Coec}(\text{NH}_3)_2]\text{Br}$ were obtained. The most stable form is the one in which the ammonia molecules occupy the *trans* positions; the other forms, which comprise two pairs of mirror images, all change over to it on standing. Morgan and Main-Smith later attempted to duplicate their own work, even in another laboratory and using new apparatus, but were unable to prepare any but the stable form.

The polynuclear complexes offer many interesting problems in stereochemistry, but very little research work has been done in this field since the time of Werner. The tetranuclear tri-(tetramminodiolcobaltic)cobaltic chloride



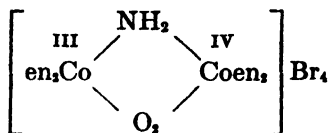
is the most interesting of these compounds from the historical point of view, for the resolution of this purely inorganic substance (94) furnished final proof of the correctness of the octahedral theory.

A polynuclear complex may contain more than one center of asymmetry. Thus, in tetraethylenediamino- μ -amminonitrodicobaltic bromide



there are two asymmetric cobalt atoms, and Werner (93) was able to obtain dextro, levo, and meso forms. The active forms were converted to the meso form by heating in solution. The fact that the meso form was completely inactive led Werner to the conclusion that there is no essential difference between "primary" and "secondary" valences. Lifschitz (47) does not agree with this conclusion.

In the peroxo salt



the two cobalt atoms differ in valence, so the compound should exist in four forms. Werner (95) isolated two of these,—the ones in which the cobalt atoms are both dextro, or both levo. Starting with the active material, Werner prepared several other optically active dinuclear complexes. These are presented in table 2. It is to be observed that all of the compounds obtained in these reactions have rotations opposite in sign to that of the original material. The rotations, also, are much smaller than that of the original μ -amino-peroxo salt. It is not clear whether this is due to a difference in structure or to partial racemization during the

TABLE 2
Reactions of $L\left[\begin{array}{c} \text{NH}_2 \\ \text{en}_2\text{Co} \diagup \quad \diagdown \text{Coen}_2 \\ \text{O}_2 \end{array} \right] \text{X}_4$
[α] = -840° ; [M] = -6854°

NO.	REAGENT	PRODUCT	[α]	[M]
1	NH ₃	$\left[\begin{array}{c} \text{III} \quad \text{NH} \quad \text{IV} \\ \text{en}_2\text{Co} \diagup \quad \diagdown \text{Coen}_2 \\ \text{O}_2 \end{array} \right] \text{X}_3$	+160°	+1372°
2	HX	$\left[\begin{array}{c} \text{HX} \\ \text{III} \quad \text{NH} \quad \text{IV} \\ \text{en}_2\text{Co} \diagup \quad \diagdown \text{Coen}_2 \\ \text{O}_2 \end{array} \right] \text{X}_3$	+192°	+1625°
3	NaI	$\left[\begin{array}{c} \text{III} \quad \text{NH}_2 \quad \text{III} \\ \text{en}_2\text{Co} \diagup \quad \diagdown \text{Coen}_2 \\ \text{OH} \end{array} \right] \text{X}_4$	+110°	+ 990°
4	HNO ₂	$\left[\begin{array}{c} \text{III} \quad \text{NH}_2 \quad \text{III} \\ \text{en}_2\text{Co} \diagup \quad \diagdown \text{Coen}_2 \\ \text{NO}_2 \end{array} \right] \text{X}_4$	+158°	+1311°
5	SO ₂	$\left[\begin{array}{c} \text{III} \quad \text{NH}_2 \quad \text{III} \\ \text{en}_2\text{Co} \diagup \quad \diagdown \text{Coen}_2 \\ \text{SO}_4 \end{array} \right] \text{X}_3$	+200°	+1384°

reactions. Werner believed that the valence of the central atom was important in determining the magnitude of rotation, as the compounds containing one tetravalent cobalt atom have somewhat larger rotations than the others. The data, however, are insufficient to support this hypothesis.

REFERENCES

- (1) ANGELL, DREW, AND WARDLAW: J. Chem. Soc. **1930**, 349.
- (2) BAILAR AND AUTEN: J. Am. Chem. Soc. **56**, 774 (1934).
- (3) BAILAR, HASLAM, AND JONES: Unpublished.
- (4) BAILAR AND JONELIS: Unpublished.

- (5) BANCROFT AND DAVIS: *J. Phys. Chem.* **35**, 1253 (1931).
- (6) BASSETT: *Annual Reports on the Progress of Chemistry*, Vol. 29, p. 92 (1932).
- (7) BECKER: Senior Thesis, University of Illinois, 1935.
- (8) BERGMANN, POLYANI, AND SZABO: *Z. physik. Chem.* **20B**, 161 (1933).
- (9) BROCKWAY AND CROSS: *J. Chem. Physics* **3**, 828 (1935).
- (10) COX: *J. Chem. Soc.* **1932**, 1912.
- (11) COX, PINKARD, WARDLAW, AND PRESTON: *J. Chem. Soc.* **1932**, 2527.
COX, PINKARD, WARDLAW, AND WEBSTER: *J. Chem. Soc.* **1935**, 459.
COX AND PRESTON: *J. Chem. Soc.* **1933**, 1089.
BOZORTH AND PAULING: *Phys. Rev.* **39**, 537 (1932).
- BRASSEUR, DE RASSENFOSSE, AND PIERARD: *Compt. rend.* **198**, 1048 (1934); *Z. Krist.* **88**, 210 (1934), and others.
- (12) COX, SHARRATT, WARDLAW, AND WEBSTER: *J. Chem. Soc.* **1936**, 129.
- (13) COX AND WEBSTER: *Z. Krist.* **90**, 561 (1935).
- (14) COX AND WEBSTER: *Z. Krist.* **92**, 478 (1935).
- (15) COX AND WEBSTER: *J. Chem. Soc.* **1935**, 731.
- (16) DICKINSON: *J. Am. Chem. Soc.* **44**, 774, 2404 (1922).
- (17) DREW: *J. Chem. Soc.* **1932**, 2328.
- (18) DREW AND HEAD: *J. Chem. Soc.* **1934**, 221.
- (19) DREW, PINKARD, PRESTON, AND WARDLAW: *J. Chem. Soc.* **1932**, 1895.
- (20) DREW, PINKARD, PRESTON, AND WARDLAW: *J. Chem. Soc.* **1932**, 1896.
- (21) DREW, PINKARD, WARDLAW, AND COX: *J. Chem. Soc.* **1932**, 988.
- (22) DREW, PINKARD, WARDLAW, AND COX: *J. Chem. Soc.* **1932**, 1004.
- (23) DWYER AND MELLOR: *J. Am. Chem. Soc.* **56**, 1551 (1934).
- (24) DWYER AND MELLOR: *J. Am. Chem. Soc.* **57**, 605 (1935).
- (25) GRÜNBERG: *Z. anorg. allgem. Chem.* **157**, 299 (1926); **164**, 207 (1927).
- (26) GRÜNBERG: *Helv. Chim. Acta* **14**, 455 (1931).
- (27) GRÜNBERG AND PTIZYN: *J. prakt. Chem.* [2] **136**, 143 (1933).
- (28) HANTZSCH: *Ber.* **59**, 2761 (1926).
- (29) HANTZSCH AND ROSENBLATT: *Z. anorg. allgem. Chem.* **187**, 241 (1930).
- (30) HEIN AND REGLER: *Naturwissenschaften* **23**, 320 (1935).
- (31) HÜRLIMANN: Thesis, University of Zürich, 1918.
- (32) JAEGER: *Optical Activity and High Temperature Measurements*. McGraw-Hill Book Co., Inc., New York (1930).
- (33) Reference 32, pp. 93 and 139.
- (34) JAEGER AND BLUMENDAL: *Z. anorg. allgem. Chem.* **175**, 161 (1928).
- (35) JENSEN: *Z. anorg. allgem. Chem.* **225**, 97 (1935).
- (36) JENSEN: *Z. anorg. allgem. Chem.* **225**, 115 (1935).
- (37) JENSEN: *Z. anorg. allgem. Chem.* **226**, 168 (1936).
- (38) JOHNSON: *Trans. Faraday Soc.* **28**, 845 (1932).
- (39) JOHNSON AND MEAD: *Trans. Faraday Soc.* **29**, 626 (1933).
- (40) KRAUS AND BRODKORB: *Z. anorg. allgem. Chem.* **165**, 73 (1927).
- (41) KUHN: IX Congr. intern. quim. pura aplicada **4**, 181 (1934).
- (42) KURNAKOW: *J. prakt. Chem.* [2] **60**, 483, 498 (1894).
- (43) LEY AND FICKEN: *Ber.* **50**, 1123 (1917).
- (44) LEY AND WINKLER: *Ber.* **42**, 3894 (1909); **45**, 372 (1912).
- (45) LIFSCHITZ: *Z. physik. Chem.* **105**, 27 (1923); **114**, 485 (1925); *Rec. trav. chim.* [4] **41**, 13 (1922).
- (46) LIFSCHITZ: *Z. physik. Chem.* **114**, 485 (1925); *Akad. Amsterdam Versl.* **33**, 661 (1924).
- (47) LIFSCHITZ: *Z. physik. Chem.* **114**, 485 (1925).

- (48) LIFSCHITZ AND FROENTJES: *Z. anorg. allgem. Chem.* **224**, 173 (1935).
- (49) LOWRY AND BURGESS: *J. Chem. Soc.* **125**, 2081 (1924).
- (50) MANN: *J. Chem. Soc.* **1926**, 2681.
- (51) MANN: *J. Chem. Soc.* **1930**, 1745.
- (52) MANN AND POPE: *Proc. Roy. Soc. London* **107A**, 80 (1925); *J. Chem. Soc.* **1926**, 2675.
- (53) MANN AND POPE: *Proc. Roy. Soc. London* **109A**, 444 (1925); *J. Chem. Soc.* **1926**, 482, 489.
- (54) MATHIEU: *Compt. rend.* **199**, 278 (1934); **201**, 1183 (1935).
- (55) MATHIEU: *Bull. soc. chim.* [5] **3**, 476 (1936).
- (56) MEER AND POLANYI: *Z. physik. Chem.* **19B**, 164 (1932).
- (57) MEISENHEIMER: *Ann.* **456**, 126 (1927).
- (58) MEISENHEIMER, ANGERMANN, HOLSTEN, AND KINDERLEN: *Ann.* **438**, 217 (1924).
- (59) MEISENHEIMER AND LINK: *Ann.* **479**, 211 (1930).
- (60) MILLS AND GOTTS: *J. Chem. Soc.* **1926**, 3121.
- (61) MILLS AND QUIBELL: *J. Chem. Soc.* **1935**, 839-46.
- (62) MORGAN AND MAIN-SMITH: *J. Chem. Soc.* **127**, 2030 (1925).
- (63) OLSON: *J. Chem. Physics* **1**, 418 (1933).
- (64) PAULING: *J. Am. Chem. Soc.* **53**, 1367 (1931).
- (65) PINKARD, SHARRATT, WARDLAW, AND COX: *J. Chem. Soc.* **1934**, 1012.
- (66) PUGH: *Biochem. J.* **27**, 480 (1933).
- (67) RAMBERG: *Ber.* **43**, 580 (1910).
- (68) REIHLEN: *Z. anorg. allgem. Chem.* **114**, 65 (1920).
- (69) REIHLEN: *Z. anorg. allgem. Chem.* **151**, 71 (1926).
- (70) REIHLEN: *Ann.* **448**, 312 (1926).
- (71) REIHLEN AND HÜHN: *Ann.* **489**, 42 (1931); **499**, 144 (1932).
- (72) REIHLEN AND HÜHN: *Ann.* **519**, 80 (1935).
- (73) REIHLEN AND NESTLE: *Ann.* **447**, 211 (1926).
- (74) REIHLEN AND NESTLE: *Ann.* **447**, 222 (1926).
- (75) REIHLEN, SEIPEL, AND WEINBRENNER: *Ann.* **520**, 256 (1935).
- (76) ROSENBLATT AND SCHLEEDE: *Ber.* **66B**, 472 (1933).
- (77) ROSENHEIM AND GERB: *Z. anorg. allgem. Chem.* **210**, 289 (1933).
- (78) ROSENHEIM AND HÄNDLER: *Ber.* **59**, 1387 (1926).
- (79) SCHLESINGER, N.: *Ber.* **58**, 1877 (1925).
- (80) SHIBATA AND TSUCHIDA: *Bull. Chem. Soc. Japan* **4**, 142 (1929).
- (81) SHIBATA, TONOKA, AND GODA: *Bull. Chem. Soc. Japan* **6**, 210 (1931).
- (82) SMIRNOFF: *Helv. Chim. Acta* **3**, 177 (1920).
- (83) SUGDEN: *J. Chem. Soc.* **1932**, 246.
- (84) TSCHERNYAEV: *Ann. inst. platine* **4**, 243, 275 (1926).
- (85) TSCHUGAEFF AND SOKOLOFF: *Ber.* **40**, 3461 (1907); **42**, 55 (1909).
- (86) TSUCHIDA, KOBAYASHI, AND NAKAMURA: *J. Chem. Soc. Japan* **56**, 1339 (1935).
- (87) TSUCHIDA, KOBAYASHI, AND NAKAMURA: *Bull. Chem. Soc. Japan* **11**, 38 (1936).
- (88) WERNER: *Z. anorg. allgem. Chem.* **3**, 316 (1893).
- (89) WERNER: *Lehrbuch der Stereochemie*, p. 344. Gustav Fischer, Jena (1904).
- (90) WERNER: *Ber.* **44**, 873 (1911); *Ann.* **386**, 1 (1912).
- (91) WERNER: *Ann.* **386**, 1 (1912).
- (92) WERNER: *Ber.* **45**, 1228 (1912).
- (93) WERNER: *Ber.* **46**, 3674 (1913).
- (94) WERNER: *Ber.* **47**, 3087 (1914).
- (95) WERNER: *Ber.* **47**, 1961 (1914).
- (96) WERNER AND SMIRNOFF: *Helv. Chim. Acta* **1**, 5 (1918).

THE ACID-BASE PROPERTIES OF COMPLEX IONS

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I. GENERAL

Although the term "complex" has been most often restricted to such particular classes of structures as the ammines, halides, etc. to which Werner gave the greater part of his attention, it is often useful to extend its meaning. Werner himself pointed out the essential similarity of such acids as H_2SO_4 , HBF_4 , and $\text{H}_2[\text{PtCl}_4(\text{OH})_2]$, and even described HCl and KOH as merely the anhydro forms of the corresponding "true" or aquo acid and base concerned. Indeed, in attempting to discuss the protolysis of ions in water solution, one is inclined to include Fe^{+++} (as $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$) and H^+ (as $[\text{H}_3\text{O}(\text{H}_2\text{O})_2]^+$) on the same terms as $[\text{Cr}(\text{NH}_3)_6]^{+++}$ and NH_4^+ . The difficulty is to find an ion to which the logically extended term "complex" does not apply. Probably such large and apparently slightly hydrated elementary ions as Cs^+ and I^- approach most nearly to this condition.

Present-day viewpoints permit a partial understanding of acid-base properties in terms of the same concepts as are necessary to account for the existence and relative stability of complex compounds,—indeed of compounds, radicals, and molecules in general. Adopting, for example, Mulliken's (30) formulation:—"Every nucleus (in a molecule) tends to be surrounded, by means of sharing or transfer of electrons, by an electron distribution corresponding to some stable configuration having a total charge approximately equal to or somewhat exceeding the charge of the nucleus";—it is evident that the vast majority of atoms have attained this state, some by the formation of "simple" ions (Na^+ , Cl^-) or molecules (C_6H_6) and others by the formation of such typical *complexes* as $[\text{Fe}(\text{CN})_6]^{---}$, $[\text{Cu}(\text{NH}_3)_4]^{++}$, HBF_4 , HSO_4^- , $[\text{S}_2]^{--}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$, or R_3NH^+ . The tendency of any particular complex to form is calculable in principle from a knowledge of the valence states of the atoms in the complex, the energies of these states, and like data for the atomic configuration which preceded the one we are studying. Tables of such valence state energies, and of relative electronegativities of atoms, have been given by Mulliken (30, 31) and others. The relative electronegativity of an atom

depends equally on its ionization potentials and its electron affinity, and the same is true of molecules. Thus any molecule or atom will have some tendency to act as an electron donor (34) (and reductant) and also as an electron acceptor (and oxidant). The balance between these tendencies determines many of the most important properties of the molecule. Electron donation or reducing character naturally tends to increase quite regularly with the negative charge on the molecule, and to change in less simple ways with its pattern and the relative charges, sizes, and polarizabilities of the atoms it contains. For a discussion of these effects Ingold's (21) recent paper in this journal may be consulted. The same author has emphasized the point that protolytic reactions are also manifestations of the same mechanisms, so that in general, where one molecule is more of a donor or reductant than another, it may also be expected to be a stronger protophile or base. The general terms "nucleophilic" and "electrophilic" are proposed to designate these tendencies.

For the student of acid-base behavior the properties of the solvent are of paramount importance. This is seen, for example, both in the formation of acids in Brønsted's sense from molecules which in themselves contain no hydrogen (cf. $\text{SO}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{O}^+ + \text{SO}_4^{--}$ and $\text{Fe}^{+++} + n\text{H}_2\text{O} \rightarrow [\text{FeOH}(\text{H}_2\text{O})_{n-2}]^{++} + \text{H}_3\text{O}^+$) and in other chemical respects, as well as in the influence it exerts through its dielectric properties on the thermodynamic properties of dissolved electrolytes.

In spite of Brønsted's success in giving to acid-base reactions a formulation sufficiently general to apply to all solvents, the great bulk of attention in this field, as in others, still remains centered upon water solutions.

It is therefore peculiarly gratifying that certain very important recent studies (2, 14, 39) have thrown new light on the peculiarities of this important solvent. Most liquids in the neighborhood of their freezing points seem to retain traces of crystalline order in the form of a "swarm" or "cybotactic" structure (38). This effect becomes much more marked when dipole interaction, hydrogen-bond formation, or resonance results in definite association into chains, as in alcohols, into polymers, as in carboxylic acids (36), or an actual tetrahedral (tridymite) structure of the swarm, as in cold water (2, 14, 39). This structure involves ionization at the ends only of any continuous chain running through the swarm, and explains the remarkably low conductivity of a substance so rich in mobile protons as water. The structure is thermolabile, so that conductance, hydrolysis, fluidity, and many other properties show a marked dependence on temperature, and is apparently also extremely sensitive to the depolymerizing effect of dissolved ions,—an effect that appears to extend over a considerable distance. According to Ulich (39) ions of sufficiently high ionic potential (Cartledge (11)) to be strongly solvated (H^+ , Li^+ , Na^+ ,

etc.) show low mobility in all solvents because of the increase in their effective radii due to solvation. The large ions like Cs^+ and ClO_4^- , which are only slightly solvated, show normal mobilities in non-aqueous solvents, but high mobilities in water. The latter phenomenon is explained by the depolymerizing effect which the ion-dipole interaction with the solvent has on the exceptionally complete swarm structure of water, so that each ion becomes surrounded by a "private space," the viscosity of which corresponds to that of depolymerized water instead of to that of the solution as a whole. Many interesting relationships are given in Ulich's paper, which should be consulted for further details.

Although the structures of such hydrates as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in the solid state have recently been shown (3) to be in excellent agreement with such views as Sidgwick's (35), it is probably still impossible to give a physical meaning to the statement that the formula of the cupric ion *in water* is $[\text{Cu}(\text{H}_2\text{O})_4]^{++}$, while that of the nickel ion is $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ (29). Such definite formulas are not at all necessary to an understanding of acid-base behavior, but are definitely a convenience as will appear below.

In solvents other than water the problems of solvation and solvolysis are at least as difficult as in water solution and have been much less studied. Kraus (24) has discussed at length the nature of the ions in these solutions and clearly indicated the difficulties of the problem.

Within very recent years the work of Sir Harold Hartley and his associates has done much to supplement the earlier researches of Goldschmidt, Walden, Franklin, Kraus, etc. on the conductance of such systems, and writers such as Sidgwick and Davies have contributed interesting suggestions.

Fundamentally, as stated above (21), the effect of different solvents on a solute depends on the relatively electrophilic or nucleophilic character of the solvent, i.e., a solvent that can act as an electron donor, base, or reducer will compete for and promote the formation of possible cations of the solute in quite a different way from one which is only an acceptor, an acid, or an oxidizing agent. Hydroxylic and other amphiprotic solvents will also have a large self-buffering action (seen to the best advantage in H_2SO_4). Also dependent on this electronegativity balance will be the dielectric constant of the solvent, which will determine the tendency to ion-association (Bjerrum, Fuoss), and in the case of protolytic equilibria will determine the gross changes in the relative strength of acids which occur when acids of different charge type are transferred from one solvent to another (7). Wynne-Jones, (42) Schwarzenbach and Egli (33), and Hammett (41) have recently shown how the less striking but very important changes of relative strength among acids of the *same charge type*

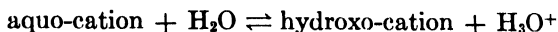
may be correlated with the structures of the acids, particularly with the electric moments of substituent groups.

A very interesting problem is presented in each solvent by the ions formed by the solvent itself. The fact that these ions have abnormal mobilities in water and some other solvents has led to two views: (1) that they are relatively little solvated, and (2) that they conduct in part by a Grotthuss chain mechanism. This latter view has been recently revived by Hückel (19) and by Fowler (2, 14) for aqueous solutions, but was adversely criticized by Kraus (24), and lately by others on the basis of results in deuterium oxide. Hammett (18), however, has redirected attention to the possibility (Latimer and Rodebush (28)) that whether or not "abnormal" mobility makes its appearance may depend on the basic strength of the solvent. Probably both the acid and basic strength of the solvent is involved, so that the phenomenon is striking in water, formic acid, and sulfuric acid (18) but less so in ammonia, pyridine, or the alcohols. The well-known effect of small quantities of water on the conductance of acids and some salts in the alcohols has recently been re-studied by Hughes and Hartley (20), who give an interesting general discussion of these effects.

II. COMPLEX METAL CATIONS

Complex ions first made their appearance in chemical theory to explain (1) the virtual disappearance of the properties of, for example, Fe^{++} ion in ferrocyanide solution, and (2) the anomalous results of transference studies in which certain usually positively charged elements apparently migrated toward the positive electrode. The real heyday of the complex compounds only began, however, with Werner's studies of the hydrates and amines. The remarkable stability of the latter led Werner to develop a powerful new theory of valency, and to enrich almost every department of chemistry with his ideas. The subject of acids and bases was often uppermost in his mind. Thus we find that his attention was attracted by a group of compounds (40) whose behavior could be explained by assuming that they contained the ten series of cations shown in table 1. On examination he found that: (1) Only the first series are able to precipitate silver oxide from silver nitrate. (2) Only the first three series liberate ammonia from NH_4^+ in the cold. (3) Only the first five series absorb carbon dioxide. (4) The first eight series react alkaline to litmus, the other two neutral. (5) The first eight series are more soluble in acetic acid than in water. From solutions of 1, 2, and 3, metallic salts precipitate aquo salts, but from solutions of 4, 5, 6, 7, and 8, hydroxo salts are precipitated. (6) All the series appear to form aquo salts with mineral acids, which are usually precipitated as such by metallic salts, but from the last two series only hydroxo salts are reprecipitated.

This beautiful group of semiquantitative results interpreted in the light of later knowledge shows: (1) The central atom confers acid strength in the diminishing order Pt^{IV} , Ru^{IV} , Cr^{III} , Co^{III} . (2) As would be expected, the total charge of the strongest base is low (+1) while the weakest has a charge of +2, but constitutive influences seem to overcome the effect of the charge in several cases. (3) The presence of aquo groups seems to increase the acid strength of the corresponding acids to an extent roughly proportional to their number. (4) The equilibrium constant (no concentrations are given) for the reaction



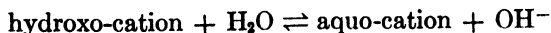
may be roughly estimated from the results reported below:

series	constant
1	10^{-6}
2-3	10^{-6} to 10^{-5}
4-5	10^{-4} to 10^{-3}
6-8	10^{-2} (circa)
9-10	10^{-2} to 10^0

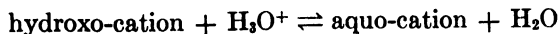
TABLE 1
Werner's series of basic cations

SERIES	CATION	SERIES	CATION
1	$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{OH}]^+$	6	$[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_3\text{OH}]^{++}$
2	$[\text{Co}(\text{NH}_3)_5\text{OH}]^{++}$	7	$[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_2(\text{OH})_2]^+$
3	$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}]^{++}$	8	$[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})\text{OH}]^{++}$
4	$[\text{Coen}_2(\text{H}_2\text{O})\text{OH}]^{++}(1, 2-)$	9	$[\text{Ru}(\text{NH}_3)_4(\text{NO})\text{OH}]^{++}$
5	$[\text{Coen}_2(\text{H}_2\text{O})\text{OH}]^{++}(1, 6-)$	10	$[\text{Pt}(\text{NH}_3)_4(\text{OH})_2]^{++}$

Largely guided by these results, Werner proposed his hypothesis that equilibria exist in solution between water, the hydroxo salts, and the corresponding aquo compounds, and later broadened this conception into a new comprehensive theory of acids and bases. The equilibria postulated by Werner may be written



and



It was natural that these mechanisms should seem to Werner of great significance and that he should have concluded that *all* metallic hydroxides are anhydro bases, becoming "true" or aquo bases only on solvation, while acids like hydrochloric he also assumed were anhydro acids. These ideas shocked the convinced followers of Arrhenius at the time, and Lamb in

1921 could write (27), "this theory has apparently found such scant acceptance that only a brief discussion of it . . . is required." Indeed, in the form proposed, Lamb was able to show that it involved "gratuitous and arbitrary assumptions" in many cases. I think it is fair to say now that the special form of the theory has no particular appeal, while many of its substantial ideas are wholly consistent with present views.

With Larson in 1920, Lamb (26) determined the relative stabilities of several cobaltic amines, finding that the dissociation into simple cobaltic ions, ammonia, and other products decreased in the order shown in table 2. The concentration dissociation constants are very small ($K_c = 2.2 \times 10^{-34}$ in the case of the hexammine), as is indicated by the well-known stability of these groups in ordinary chemical operations. It is, of course,

TABLE 2
Relative stabilities of cobaltic amines

(1) $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+(1,6-)$	(4) $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+(1,2-)$
(2) $[\text{Co}(\text{NH}_3)_5]^{+++}$	(5) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+++}$
(3) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{++}$	(6) $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+++}$

TABLE 3
Dissociation constants of amines

AMMINE	K_a
$\text{Ag}(\text{NH}_3)_2^+$	6.8×10^{-8}
$\text{Cu}(\text{NH}_3)_2^+$	1.5×10^{-9}
$\text{Cd}(\text{NH}_3)_4^{++}$	1.0×10^{-7}
$\text{Zn}(\text{NH}_3)_4^{++}$	2.6×10^{-10}
$\text{Co}(\text{NH}_3)_6^{++}$	1.25×10^{-8}

to be expected that those cations with the greatest tendency to liberate ammonia should be the weakest acids and this is in general the case, as indicated in table 6. The same authors also determined the dissociation constant of *cobaltous* hexammine, and give the list shown in table 3 for comparison. These complexes, being much more highly dissociated, should evidently be still weaker acids.

Much work has been done on the vapor tensions of amines, and a particularly interesting series of results is given by Spacu and Voichescu (37). In a study of certain ammoniates of the thiocyanate, formate, acetate, chromate, glycolate, and other salts of Cu^{++} , the strength of the bond between the metal ion and ammonia was found to be inversely proportional to the base strength of the anion of the salt, under otherwise comparable conditions, while many other structural influences were also apparent.

Bjerrum (4), in 1906, gave 0.89×10^{-4} as the constant at 25°C. of the reaction



and Denham (12), in 1908, gave a value about twice as great. With Fonda (25), Lamb made several determinations of this quantity, arriving at an average value of 1.58×10^{-4} at 25°C. The later determination by Brønsted and Volqvartz (9) lies in the same range.

A broader attack on the acidity problem was made in collaboration with Victor Yngve (27). Lamb and Yngve determined the conductance ratio $\alpha = \frac{\lambda_v}{\lambda_0}$ for a series of hydroxides of cobaltammine cations at 0°C., finding that many of the bases were apparently as highly ionized as the hydroxides of the alkalis. Their series is presented in table 4. These

TABLE 4
Conductance ratio of a series of hydroxides of cobaltammine cations

NO.	CATION	α (PER CENT) ($1.33 \times 10^{-3}M$)	α' (PER CENT)
1	$[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$	97.6	
2	$[1,6\text{-Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	95.0	
3	$[\text{Co}(\text{NH}_3)_6]^{+++}$	89.5	
4	$[\text{Co}(\text{en})_3]^{+++}$	88.6	
5	$[1,2\text{-Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$	81.2	
6	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+++}$	53.5	82.9
7	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})(\text{NO}_2)_2]^+$	36.0	
8	$[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{+++}$	27.3	84.8
9	$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+++}$	24.6	74.0

values are for the hydroxides of the cations as written. If the more probable assumption (rejected by Lamb) is made, that the aquo-cations are transformed to hydroxo compounds in Werner's sense, the more useful figures (α') in the third column are obtained.

Brønsted (8) has called attention to the importance on the one hand of the number of dissociable protons in the acid and on the other of the number of possible points of attachment on the conjugate base. This "statistical factor" appears useful in harmonizing the results of catalytic studies with bases of different charge type (10), although it is not sufficient to explain the whole difference in strength found in a series of otherwise similar trivalent cation acids (Brønsted and Volqvartz (9)).

The last paper referred to is almost the only serious modern attempt that has been made to determine accurately the relative strength of a series of multiply charged cation acids. The substances studied with their dissociation constants at 15°C. are supposedly the tripositive ions (see

TABLE 5
Brønsted and Volqvartz's series of tripositive acids

NO.	ION	$K_a \times 10^4$	NO.	ION	$K_a \times 10^4$
1	$\left[\text{Co} \begin{smallmatrix} \text{H}_2\text{O} \\ (\text{NH}_3)_5 \end{smallmatrix} \right]$	2.04	5	$\left[\text{Rh} \begin{smallmatrix} \text{H}_2\text{O} \\ (\text{NH}_3)_5 \end{smallmatrix} \right]$	1.38
2	$\left[\text{Co} \begin{smallmatrix} (\text{H}_2\text{O})_2 \\ (\text{NH}_3)_4 \end{smallmatrix} \right]$	6.03	6	$[\text{Al}(\text{H}_2\text{O})_6]$	11.2
3	$\left[\text{Co} \begin{smallmatrix} (\text{H}_2\text{O})_3 \\ (\text{NH}_3)_3 \end{smallmatrix} \right]$	18.8	7	$[\text{Cr}(\text{H}_2\text{O})_6]$	126.
4	$\left[\text{Co} \begin{smallmatrix} (\text{H}_2\text{O})_4 \\ (\text{NH}_3)_2 \end{smallmatrix} \right]$	400.	8	$[\text{Fe}(\text{H}_2\text{O})_6]$	6300.

TABLE 6
Summary of results on the acid strength of the ammino cations

ACID	pK_a (Lamb (0°C.))	pK_a (Werner)	pK_a (Brønsted (15°C.))
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$			
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{+ (1,6-)}$			
$[\text{Co}(\text{NH}_3)_6]^{+++}$			
$[\text{Co}(\text{en})_3]^{+++}$			
$[\text{Co}(\text{NH}_3)_5\text{OH}]^{++}$			
$[\text{Co}(\text{en})_2(\text{OH})_2]^+$	(13)		
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^{+ (1,2-)}$			
$[\text{Co}(\text{NH}_3)_4(\text{OH})_2]^+$	(12)		
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2(\text{H}_2\text{O})]^+$	(11)		
$[\text{Co}(\text{NH}_3)_4(\text{NO}_2)(\text{H}_2\text{O})]^{++}$		(6)	
$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+++}$			5.86
$[\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_2]^{++}$	5.72 (20°C.)	5.42 (Bj.)	
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+++}$		(5-6)	5.69
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+++}$		(5-6)	5.22
$[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{+++ (1,2-)}$		(3-4)	
$[\text{Co}(\text{en})_2(\text{H}_2\text{O})_2]^{+++ (1,6-)}$		(3-4)	
$[\text{Al}(\text{H}_2\text{O})_6]^{+++ (?)}$			4.95
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{+++}$			4.73
$[\text{Cr}(\text{H}_2\text{O})_6]^{+++ (?)}$	3.80 (25°C.)	4.05 (Bj.) 3.75 (D.)	3.90
$[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{+++}$			3.40
$[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4\text{OH}]^{++}$		(2-3)	
$[\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{+++}$		(2-3)	
$[\text{Co}(\text{NH}_3)_2\text{py}_2(\text{H}_2\text{O})_2]^{+++}$		(2-3)	
$[\text{Ru}(\text{NH}_3)_4\text{NOH}_2\text{O}]^{+++}$		(2)	
$[\text{Pt}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+++}$		(2)	
$[\text{Fe}(\text{H}_2\text{O})_6]^{+++ (?)}$			2.20

In this table (Bj.) refers to Bjerrum (4) and (D.) to Denham (12).

table 5). It will be noted that Nos. 1 and 2 relate to Werner's series 2 and 3 (table 1) and that the constants actually determined in these cases fall within the limits indicated by Werner's work.

The calculated influence of the statistical factor is in direct agreement with the first four values given, but is insufficient to account for the gradations found. The authors estimate the residual "chemical" effects on the strength as increasing in the ratio 1:1.5:3.3:50. If the statistical factor proves to be universally important, it may later be possible from such results as these to calculate back from the observed strength or catalytic constants of a series of hydrates and determine the relative number of water molecules bound in the coordination complex. Thus in the present case better agreement would be secured by assuming a structure $[\text{Al}(\text{H}_2\text{O})_4]^{+++}$ for the Al^{+++} ion. Brønsted and Volqvartz (9) also determined the salt effects on the constants listed and found them very large in agreement with prediction.¹

Table 6 gives an attempt to summarize the results of the work reported above on the acid strength of the ammino-cations. A few hydrate complexes are included for comparison.

It is evident that the usual influences such as charge and size of the complex, charge of the central atom, and the statistical factor are operating here. No certain conclusions can be drawn concerning the relative effect of the different anions within the complex, although the weakest acid of the whole list contains the very strong base CO_3^{--} . The ammino-cations are in general far less acid than the corresponding aquo-cations, as well as far more stable.

Quite recently (15) it has been found that of the isomeric complexes $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$, the *trans* isomer is much the stronger base, and that the difference between the first and second hydroxyl is much sharper than in the *cis* complex.

III. THE ACIDITY OF HYDRATES

It has not seemed worth while to present a complete table of results on the hydrolysis of metallic salts, because (1) the results are relatively familiar, (2) the exact structure of the acids concerned is for the most part unknown, and (3) there is a fairly satisfactory qualitative theory of the effects concerned.

Many authors have discussed the effect of charge and size of a simple cation on the acidity of its oxide and hydroxide, and Cartledge (11) has developed an expression for the ionic potential which has been applied by Brintzinger (6) to the hydration of cations in solution. This and other aspects of Brintzinger's work have, however, been destructively criticized by Schmitz-Dumont (32).

¹ A recent modification by Pedersen of the theory of the statistical factor seems to be controverted by recent studies in heavy water (43).

The hydrolysis of a great many salts in solution has been measured by a variety of means, and the results are to be found in tables such as those of Landolt-Börnstein. Some of the best work in this field has been done by Bjerrum. A large number of rare earth cations were studied at the University of Illinois by Kleinheksel and Kremers (22).

IV. ONIUM SALTS AS ACIDS

Since the great work of Bredig (5) on the hydrolysis of the organic ammoniums, little of fundamental importance has been done on the relation of structure to acid strength of these groups in water solution. Hall and Sprinkle (16) called attention to a few new regularities in this field, and two extremely interesting contributions by Hammett have greatly extended the possibilities of further advance. In one (17) he showed how the acid strength of extremely strong indicator acids could be quantitatively studied, and in the other (13) extended the method to colorless substances by the use of ultra-violet colorimetry. The special properties of the hydronium ion $H^+(H_2O)_n$ are discussed by Rodebush in another paper in this symposium.

That the onium compounds may be acids not only in solution, but also in the fused state has been emphasized in valuable papers by Audrieth (1).

V. COMPLEX ANIONS

While a few anions of low charge are acidic in water, the overwhelming majority are either neutral or distinctly basic. Since structural influences on the strength of the uncharged acids have been so often discussed, only brief mention of them will be made here.

Many of the common anions contain a central atom, such as chlorine or iron, and varying numbers of atoms or groups coördinated with it.

Hantzsch remarked that among the oxygen acids those with the most oxygen were in general the strongest, and that, as a rule, complex anions tend to be weak bases. Since the mechanism of solvation and solvolysis is different with anions and cations, it is reasonable to expect those anions whose central atoms are coördinatively saturated to attract the hydrogen of water relatively weakly and to undergo less basic hydrolysis, just as the amines and similarly saturated cations show but slight acid properties. Of course, the influence of the charge is as usual all important. In two recent papers Kolthoff and Tomsicek (23) have brought to light the striking fact that while $[Fe(CN)_6]^{---}$ and $[Mo(CN)_6]^{----}$ are very weak bases, $[Fe(CN)_6]^{----}$ is about as strong a base as benzoate ion.

REFERENCES

- (1) AUDRIETH, L. F., LONG, A., AND EDWARDS, R. E.: J. Am. Chem. Soc. **58**, 428-9 (1936) (references to earlier papers).
- (2) BERNAL, J. D., AND FOWLER, R. H.: J. Chem. Physics **1**, 515 (1933).

- (3) BERNAL, J. D., AND WELLS, A. F.: Chem. Soc. Ann. Repts. **32**, 222 (1935).
- (4) BJERRUM, N.: Kgl. Danske Videnskab. Selskabs Skrifter [7] **4**, 1 (1906).
- (5) BREDIG, G.: Z. physik. Chem. **13**, 191 (1894).
- (6) BRINTZINGER, H.: Z. anorg. allgem. Chem. 1933-36, many papers.
- (7) BRØNSTED, J. N., numerous papers, e.g., BRØNSTED, J. N., DELBANCO, A., AND TOVBORG-JENSEN, A.: Z. physik. Chem. **169A**, 361-78 (1934).
- (8) BRØNSTED, J. N.: Chem. Rev. **5**, 231-338 (1928). See especially p. 322 ff.
- (9) BRØNSTED, J. N., AND VOLQVARTZ, K.: Z. physik. Chem. **134**, 97-134 (1928).
- (10) BRØNSTED, J. N., AND VOLQVARTZ, K.: Z. physik. Chem. **155A**, 211-24 (1931).
- (11) CARTLEDGE, G. H.: J. Am. Chem. Soc. **50**, 2855 (1928); **52**, 3076 (1930).
- (12) DENHAM, H. G.: J. Chem. Soc. **93**, 53 (1908).
- (13) FLEXSER, L. A., HAMMETT, L. P., AND DINGWALL, A.: J. Am. Chem. Soc. **57**, 2103 (1935).
- (14) FOWLER, R. H., AND BERNAL, J. D.: Trans. Faraday Soc. **29**, 1049 (1933).
- (15) GRINBERG, A. A., AND RYABCHIKOV, D. I.: Compt. rend. acad. sci. U. S. S. R. (N. S.) **4**, 259-262 (1936); Chem. Abstracts **30**, 3701 (1936).
- (16) HALL, N. F., AND SPRINKLE, M. R.: J. Am. Chem. Soc. **54**, 3469-85 (1932).
- (17) HAMMETT, L. P., AND DEYRUP, A. J.: J. Am. Chem. Soc. **54**, 2721-39, 4239-47 (1932).
- (18) HAMMETT, L. P., AND LOWENHEIM, F. A.: J. Am. Chem. Soc. **56**, 2620-5 (1934).
- (19) HÜCKEL, E.: Z. Elektrochem. **34**, 546 (1928).
- (20) HUGHES, O. I., AND HARTLEY, H.: Phil. Mag. **15**, 610 (1933).
- (21) INGOLD, C. K.: Chem. Rev. **15**, 225-74 (1934).
- (22) KLEINHEKSEL, J. H., WITH KREMERS, H. C.: J. Am. Chem. Soc. **50**, 965 (1928).
- (23) KOLTHOFF, I. M., AND TOMSICEK, W. J.: J. Phys. Chem. **39**, 945-55 (1935).
- (24) KRAUS, C. A.: Properties of Electrically Conducting Systems. The Chemical Catalog Co., Inc., New York (1922).
- (25) LAMB, A. B., AND FONDA, G. R.: J. Am. Chem. Soc. **43**, 1154-78 (1921).
- (26) LAMB, A. B., AND LARSON, A. T.: J. Am. Chem. Soc. **42**, 2024-46 (1920).
- (27) LAMB, A. B., AND YNGVE, V.: J. Am. Chem. Soc. **43**, 2352-66 (1921).
- (28) LATIMER, W. M., AND RODEBUSH, W. H.: J. Am. Chem. Soc. **42**, 1432 (1920).
- (29) MOELWYN-HUGHES, E. A., AND SHERMAN, A.: J. Chem. Soc. **1936**, 101-10.
- (30) MULLIKEN, R. S.: Phys. Rev. **41**, 60 (1932).
- (31) MULLIKEN, R. S.: J. Chem. Physics **2**, 782 (1934).
- (32) SCHMITZ-DUMONT, O.: Z. anorg. allgem. Chem. **226**, 33-45 (1935).
- (33) SCHWARZENBACH, G., AND EGLI, H.: Helv. Chim. Acta **17**, 1176-96 (1934); **18**, 5-6 (1935).
- (34) SIDGWICK, N. V.: The Electronic Theory of Valency, p. 116. Oxford University Press, London (1927).
- (35) Reference 34, p. 195.
- (36) SIDGWICK, N. V.: Chem. Soc. Ann. Repts. **31**, 40 ff. (1933).
- (37) SPACU, G., AND VOICHESCU, P.: Z. anorg. allgem. Chem. **226**, 273-88 (1936).
- (38) STEWART, G. W.: Trans. Faraday Soc. **29**, 982, 1077 (1933).
- (39) ULICH, H.: Z. angew. Chem. **49**, 279-83 (1936).
- (40) WERNER, A.: New Ideas on Inorganic Chemistry (translated by E. P. Hedley), p. 201. Longmans, Green, and Co., London (1911).
- (41) WOOTE, I. A., AND HAMMETT, L. P.: J. Am. Chem. Soc. **57**, 2289-96 (1935).
- (42) WYNNE-JONES, W. F. K.: Proc. Roy. Soc. London **140A**, 440 (1933).
- (43) WYNNE-JONES, W. F. K.: Chem. Rev. **17**, 119 (1935).

HALOGENATED HYDROCARBON SOLVENTS

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Halogenated hydrocarbons, especially the chlorinated derivatives, have been finding extensive use in degreasing, dewaxing, dry cleaning, extraction, and similar operations. A number of patents have been issued on uses in these fields. For instance, Farrington (36) has covered non-inflammable mixtures of petroleum naphthas with carbon tetrachloride as cleaning fluids. Another patent (60) deals with cleaning fluids containing less than 37.5 to 40.5 per cent of ethylene dichloride and more than 59.8 to 62.5 per cent of carbon tetrachloride. Other dry-cleaning fluids covered are aliphatic saturated unsymmetrical polychloro substitution products (67), a mixture (14) containing 1 per cent of tetrachloroethane, 3 to 5 per cent of dichloroethyl ether, 6 to 4 per cent of carbon tetrachloride, and 90 per cent of Stoddard solvent, and a mixture (71) containing 4 per cent of tertiary-amyl alcohol, 16 per cent of ligroin, and 80 per cent of carbon tetrachloride. An interesting patent (68) describes a non-inflammable solvent mixture comprising a non-inflammable solvent and an inflammable substance of the same volatility as the non-inflammable solvent, so that no appreciable fractionation occurs when the solvent is evaporated. A paint and varnish remover has been described which contains a mixture of solvents including a volatile inflammable solvent and a volatile non-inflammable solvent, composed of trichloroethylene, the proportion of trichloroethylene being sufficient to suppress the inflammability of the former so that the composition does not ignite, together with some wax.

Dry-cleaning fluids containing 0.1 to 3 per cent of a "lusterizing" agent such as chlorinated naphthalene in chlorinated solvents have been disclosed (67a). Another cleaning solvent contains a naphtha of 290–325°F. boiling range with acetylene tetrachloride to yield a non-inflammable composition (68b). A mixture of naphtha having a boiling range of 160–230°F. with 60 to 65 parts of carbon tetrachloride also has been recently proposed (68a). Still another cleaning solvent comprises 10 to 20 per cent of a petroleum distillate boiling at 70–134°C., 20 to 88 per cent of carbon tetrachloride, and 2 to 70 per cent of tetrachloroethylene (26a). This mixture is claimed to be non-explosive in all boiling ranges.

In one patent (66a) a flame-resistant solvent is produced by intensively chlorinating a mixture of gaseous hydrocarbons, removing a fraction boiling at 60–310°F., and blending it with 5 to 60 per cent of a petroleum fraction having distillation characteristics similar to that of the selected fraction.

PREPARATION

A large number of methods are available for the preparation of halogenated solvents. At the present time chlorinated hydrocarbons appear to have the greatest commercial significance, and most of the literature deals with these derivatives. Carbon tetrachloride is generally prepared by the interaction of carbon disulfide with sulfur dichloride (1, 38) in the presence of iron, while chloroform is obtained by treating carbon tetrachloride with steam in the presence of iron. This is peculiar in view of the fact that cheap methane is available and that all of its chlorine derivatives can be separated by fractionation. Very likely the reason is that the present process does not involve much loss of chlorine as hydrogen chloride. A number of patents have been issued covering improved methods of direct chlorination of saturated hydrocarbons (24, 25, 32, 41, 42, 56). Possibly some commercial processes will be developed wherein the hydrogen chloride may be utilized in other syntheses. Methylene chloride has been prepared by the chlorination of methyl chloride (43).

Photochemical chlorination of methane is reported to give up to 29 per cent of chlorine going to methyl chloride (80 per cent of the total chlorine being utilized), the methane to chlorine ratio varying from 15:1 to 19:1. The energy utilization, however, is low (57a). The removal of chlorinated products, followed by recycling of unreacted hydrocarbons, has likewise been disclosed in the literature (43a). Continuous removal of hydrogen chloride is provided for where the substance is detrimental (42a). In another modification, the chlorinated products are removed and the remainder mixed with fresh feed and chlorinated (44a). The hydrogen chloride from the reaction products may also be treated directly with methanol in the presence of a catalyst to produce methyl chloride (41a).

The two-carbon atom derivatives are mostly derived commercially from ethylene and acetylene. According to Curme (23), the best way of preparing ethylene dichloride is to react the liquid chlorine and ethylene at the vapor pressure of chlorine. It is also obtained as a by-product in the production of ethylene glycol. Other methods for producing this product have also been reported (11, 35, 39, 53, 54, 69). According to Maier (53) the chlorination of ethylene at 25°C. produces 70 per cent of trichloroethane, 15 per cent of ethylene dichloride, 5 per cent of tetrachloroethane, and 10 per cent of higher chlorinated products. Ethylene reacts readily with

hydrogen chloride to produce ethyl chloride (12, 54, 59, 70, 72, 73, 74). This product may be further chlorinated. The treatment of alcohol with hydrogen chloride will also produce ethyl chloride (44).

Acetylene is a valuable raw material for the preparation of chloro derivatives. By chlorination it is converted to tetrachloroethane (54), which yields *sym*-dichloroethylene on treatment with iron or zinc, or trichloroethylene on treatment with slaked lime (7, 64). The chlorination of trichloroethylene gives pentachloroethane, which on treatment with slaked lime gives perchloroethylene. Trichloroethane may also be prepared by the chlorination of vinyl chloride (45, 48) or by chlorinating acetylene in the presence of hydrogen chloride (46). In the latter case a 90 to 98 per cent yield of product is obtained having the following composition: 10 to 15 per cent of dichloroethylene, 60 to 70 per cent of trichloroethane, 10 to 25 per cent of acetylene tetrachloride, 0 to 5 per cent of higher products. Dichloroethylene may also be prepared by direct chlorination of acetylene (47, 57), and by treating acetylene with tetrachloroethane in the presence of a hydrogenation catalyst at 350°C. (19a). Ethylidene chloride has been produced by treating vinyl chloride with hydrogen chloride (26).

In one patent (27a) chlorine is reacted with a saturated aliphatic hydrocarbon of three to five carbon atoms to form a mixture of saturated chlorohydrocarbons, hydrogen chloride, and olefins. The latter two products are then reacted at a temperature below 200°C. The formation of dichloroethylene derivatives is claimed when chlorine is reacted with a mixture of trichloro- and tetrachloro-propanes and -butanes (70a). Cracked gases have been likewise chlorinated in two stages (23d), the more reactive hydrocarbons (unsaturates) being reacted in the first stage. Substitution of halogen in paraffin hydrocarbons, and addition of halogen to olefins has been effected simultaneously in a mixture of hydrocarbons by the action of free halogen in the absence of oxygen in the dark at below 100°C. (64a).

Isopropyl chloride (16, 17), *n*-propyl chloride (50), propylene dichloride (30), butyl chlorides, (22, 61), and chlorinated acid extract (34) have also been prepared as raw materials for this purpose. Commercial chlorination of pentanes (9, 10, 20) has made available a large supply of monochloro derivatives and by-product dichloropentanes. According to some investigators (72a), chlorination of pentane, hexane, and heptane (unlike the case of aromatics) is not accelerated by antimony pentachloride.

Cyclic chlorinated hydrocarbons are used as solvents to a certain extent in industry. Direct chlorination is usually resorted to in the presence of catalysts, such as in presence of a copper catalyst at 300°C. (49, 59a), in the vapor phase at high temperature with aluminum, copper, iron, and cerium (55a, 72b), also with sulfur, antimony chloride, and lead (28a). Monochloro aromatic hydrocarbons have also been further chlorinated to

TABLE 1
Experimental data

FRACTION °F.	PER CENT OF TOTAL	SPECIFIC GRAVITY	COLOR AFTER NEUTRALIZATION	INSTABILITY ^j		K.B. SOLVENT POWER		BURNING TEST
				After neutrali- zation	After hydrol- ysis	After neutrali- zation	After hydrol- ysis	
Charge—hydro solvent ^a								
158-230	15	0.8270	Water white					Yes ^f
230-284	22	0.8808	Water white					Yes
284-338	30.6	0.9643	Green		385	76.7	77.4	No
338-345	23	1.0846	Brown					No
Residue	9.4		Black					
Charge—stabilizer bottoms ^b								
104-230	3.7							Yes
230-272	17.3	0.916						Yes
272-292	18.7	0.985						Barely
292-320	17.3	1.056				76.4 ^c	75.4 ^c	No
320-374	31.1	1.167		206 ^d				No
Charge—stabilizer bottoms ^e								
To 230	0							
230-278	6.7							Yes
278-320	37.3	1.0137		496	460	73.9		No
320-374	42.7	1.0827			520			No
374-410	12.0	1.1626						No
Residue and loss	1.3							
Charge—commercial amyl chlorides ^a								
To 230	58.6	0.8725	Colorless					Yes
230-266	2.6		Colorless					Yes
266-320	22.8	1.077	Colorless	630	565	82		No
320-370	11.1	1.147	Colorless	430	423			No
370-410	2.9	1.296	Colorless					No
Residue	2.0							
Charge—Edeleanu extract ^h								
300-350 ⁱ			Colored	65				No

(a) B.P. 176-212°F. K.B. value = 57.9. Chlorinated to 20 per cent Cl at 185°F.

(b) Contains about 67 per cent pentanes and pentenes, 26 per cent hexanes and hexenes, and 7 per cent boiling in heptane range, total unsaturates being about 35 per cent. Chlorinated to 38.5 per cent (sp. gr. 1.090).

(c) For combined fractions 272-374°F.

(d) For combined fractions 375-450°F.

(e) Same as (b) treated with 20 per cent by volume of concentrated sulfuric acid.

(f) "Yes" in burning test means that sample will flash when lighted match is passed over surface on glass plate.

(g) Mixture of commercial amyl monochlorides. Chlorinated at 180°F. for 4½ hours in glass to 0.8715-0.9835 sp. gr.

(h) B.P. 340-430°F. Chlorinated at 60-70°F. to 39 per cent Cl.

(i) At 2 mm.

(j) Ten cc. refluxed with 25 cc. water for 2 hrs. and titrated with 0.1 N caustic.

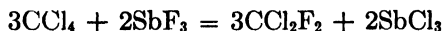
produce higher boiling products (32a, 71a). In the preparation of chlorotoluene, it has been pointed out (48a) that direct chlorination at 250–600°C. without catalysts results in substitution entirely in the side chain, whereas catalysts direct the reaction towards nuclear chlorination.

Experimental data on the chlorination of various petroleum products are presented in table 1. In order to obtain the best yields, it has been found desirable to chlorinate in glass vessels in the absence of iron with good dispersion of the chlorine and hydrocarbon. A reflux condenser may be attached to avoid evaporation of the lighter fractions. Very good yields of the lower boiling chlorides were obtained, especially in view of the fact that the low-boiling inflammable fractions may be rechlorinated without difficulty. In the case of sulfur dioxide extract, the presence of the heavier fraction produced considerable coking, so that only the light fraction (50 per cent) was found to give satisfactory results.

The lower boiling gasoline polychlorides are satisfactory for certain types of outside paints and preparations where non-ignitability is of prime importance. They also have possibilities in dewaxing and other uses.

With recent advances in chlorination technique (21, 51, 65) there is a possibility of improving the stability of chlorinated higher hydrocarbons by selective direction of the chlorine with special solvents, peroxides, etc.

Fluorinated hydrocarbons (13) and similar aliphatic products have also been described (3, 4, 5, 8, 15, 18, 31, 37, 38a, 52, 58). They are generally prepared by reacting a chlorinated hydrocarbon with antimony trifluoride, such as by the reaction:



SOLVENCY

The solvent power of most paint and varnish solvents is expressed as per cent of benzene (benzol) solvency by the kauri butanol test (2, 11a). This test, of course, determines the solvent action on gum kauri, and although it has proved to be a good indicator for general purposes, its merit may not be as great in the dry-cleaning and other industries.

Generally, it may be stated that halogenation improves the kauri butanol value of hydrocarbons, although there appears to be an exception in the case of fluoro aromatics. The effect of halogenation on aromatic hydrocarbons is shown by the following data:

Compound	K. B. solvent power per cent
Benzene.....	100.0
Bromobenzene.....	128.8
Chlorobenzene.....	115.2
Fluorobenzene.....	93.0

Chlorination of aromatics and their homologs raises the kauri butanol solvent power, but not to as high an extent as in the case of the aliphatics. Some results obtained are as follows:

<i>Compound</i>	<i>K. B. solvent power per cent</i>
Benzene.....	100.0
Chlorobenzene.....	115.2
Toluene.....	93.8
<i>o</i> -Chlorotoluene.....	108.8

In the case of the saturated aliphatic hydrocarbons having two to eight carbon atoms per molecule, the effect of chlorination seems to be fairly definite (within a few kauri numbers) and might be given as follows:

<i>No. of Cl atoms per molecule</i>	<i>K. B. solvent power per cent</i>
0	25
1	60
2	82
3	100 (approx.)

Methane, however, is an exception. In this case chlorination raises the solvency markedly, until all of the hydrogen is replaced with chlorine, when a sudden drop in solvency results:

<i>Compound</i>	<i>K. B. solvent power per cent</i>
Dichloromethane.....	116.0
Chloroform.....	156.7
Carbon tetrachloride.....	92.1

As shown in table 1, non-inflammable chlorinated petroleum hydrocarbons of 75 kauri butanol solvent power may be prepared in high yields. It has been found that refluxing with caustic generally improves the kauri butanol solvent power (probably owing to the formation of hydroxyl groups), while ordinary steam distillation has a tendency to decrease the kauri butanol value somewhat, possibly because of dechlorination.

STABILITY

For many purposes, e.g., preparation of metal paints, dry-cleaning solvents, etc., it is essential that the solvent employed should not produce excessive acidity. On the other hand, in many uses, notably in the outside paint industry, this element is not of such marked importance, since the small amount of acidity produced would not be very injurious to the concrete, wood, brick, and other substantially inert material coated, provided the proper containers are used.

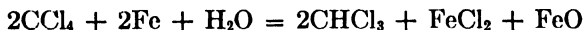
The test for instability employed herein consists in refluxing 10 cc. of

the solvent with 25 cc. of water for 2 hours, and titrating the free acidity with 0.1 *N* caustic. Although it is not exactly comparative, it is sufficiently satisfactory to give a good indication of the relative instability of the product in the presence of water. Iron generally greatly accelerates the decomposition of moist chlorinated products, while oil tends to decrease it in most cases.

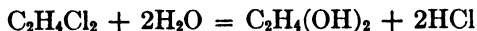
As a general rule, the bromides are less stable than the chlorides, while the fluorides are considered more stable.

The tests reported in table 2 indicate that the chlorine attached to a primary aliphatic carbon atom is much more stable than that on the secondary, which is in turn more stable than that on the tertiary. That is why the methyl and ethyl derivatives, such as carbon tetrachloride and ethylene dichloride, are relatively so much more stable than other aliphatic chloro derivatives. The tendency in ordinary chlorination is to form the least stable chloride if the groups are available. In the case of the higher homologs, adjacent chlorine atoms, such as those produced by the usual chlorination of unsaturates, produces a very unstable molecule which tends to split off hydrogen chloride to give a more stable unsaturated derivative. The reaction may be carried out by steam distillation of the compound. Refluxing with caustic often effects this, although the usual tendency is to produce a hydroxyl group. Propylene chloride possesses a high degree of stability in spite of the presence of a secondary carbon atom.

In the case of carbon tetrachloride it must be remembered that, in the presence of iron, iron oxide is deposited according to the reaction:



This is in addition to the true hydrolysis, which is apparently the main reaction undergone by most of the higher homologs:



The rate of hydrolysis appears to increase for these compounds in the following order: trichloroethylene, carbon tetrachloride, ethylene dichloride.

According to Dickinson and Leermakers (23b), photooxidation of tetrachloroethylene in carbon tetrachloride is strongly inhibited by oxygen. In the presence of both chlorine and oxygen, photosensitized oxidation to trichloroacetyl chloride, and to some extent to phosgene, occurs.

The chlorinated aromatics, i.e., those which have the chlorine attached directly to the nucleus, are considered to be very stable compounds, while the naphthenic chlorides appear to be exceptionally unstable.

A large number of proposals have been made for inhibiting the decom-

TABLE 2
Data on halogenated hydrocarbon solvents

[illegible]

(a) At 12.5°/40°C. (b) Mixture of isomers *b*, *pa*, 48°C, and 60°C. (c) Dissolves 1 per cent sulfur. (d) Commercial mixture of isomers, stabilizer bottoms. (e) From chlorination of hydrogenated solvent *b*, 176–212°C. (f) Burns with difficulty. (g) At 2 mm. (h) At 16°/15°C. (i) Gasoline = 2.3; carbon disulfide = 24.3. (j) At 23°C. (k) Gasoline = 15; 27–212°C. Hydro solvent = 58; benzene = 100. (l) At -28.7°C. (m) Will not burn even on boiling in open crucible. (n) At 56°C. (o) Sublimes. (p) At 55°C. (q) Inflammability limits 9.7 to 12.8 per cent. (r) Inflammability limits 3 to 14 per cent. (s) Ten cc. reduced viscosity with 25 cc. of water for 2 hrs. and titrated with 0.1 *N* caustic.

position of chlorinated hydrocarbons. Most of the methods involve the addition of basic or unstable materials such as amines (6, 23c), gums (27), dyes (28), hydrocarbons (29, 62), etc., but they generally involve the neutralization or addition of the liberated hydrochloric acid rather than a true inhibition of the decomposition. Carlisle and Levine (19) state that trichloroethylene will not decompose in the light unless oxygen is present and recommend the addition of small amounts of anti-oxidants. However, in many cases, as in the dry-cleaning industry, the solvents must be recovered by distillation, involving the loss of inhibitor which is generally much higher boiling. The decomposition of methylene chloride was reported to be effected to a great extent by the amount of water present (19).

TABLE 3
Ignitable concentrations of mixed solvents

A	B	PERCENT A WHEN MIXTURE			
		Flashes and burns	Burns only	Ignites immediately	Will not ignite immediately
Acetylene tetrachloride	Ethyl acetate	20-40	50	60	70
Acetylene tetrachloride	Isopropyl alcohol	30	40-50	60	65
Carbon tetrachloride	Isopropyl alcohol			20	30
Carbon tetrachloride	Ethylene dichloride				25
Carbon tetrachloride	Ethyl acetate	30		40	50
Carbon tetrachloride	Benzene				70
Carbon tetrachloride	Gasoline				65
Methylene chloride	Ethylene dichloride				40
Trichloroethylene	Benzene				67
Trichloroethylene	Stoddard solvent				50
Trichloroethylene	Ethylene dichloride				65

It seems that the problem might be somewhat simplified if the more stable fluorides were made available at a low price. This, of course, applies only for cases requiring exceptionally stable solvents. Even in the case of these solvents, corrosion of copper and other metals has been encountered in "long-life" equipment such as refrigerator systems, although this is claimed to be minimized by the use of white oil and other special lubricants.

INFLAMMABILITY

For ordinary purposes, chlorinated solvents should be satisfactory if they do not ignite at room temperatures when momentarily exposed in thin films to flames. However, in many cases it is necessary to employ materials which will not ignite at elevated temperatures, and in such cases highly

TABLE 4
Flash points of mixed solvents

A	PER CENT A	B	PER CENT B	ORIGINAL FLASH POINT
				^{°F.}
Trichloroethylene	80	Naphtha (72°)	20	180
Trichloroethylene	75	Benzine	25	180
Trichloroethylene	50	Kerosene	50	90
Trichloroethylene	67	Benzene (benzol)	33	187-90
		Turpentine	100	120
Trichloroethylene	75-83	Turpentine	17-25	192-5
Trichloroethylene	50	Stoddard solvent	50	None at 202
Trichloroethylene	75	Acetone	25	Below 34
Trichloroethylene	95	Acetone	5	70
Trichloroethylene	90	Acetone	10	45
Trichloroethylene	95	Isopropyl alcohol	5	75
Trichloroethylene	90	Isopropyl alcohol	10	65
Trichloroethylene	95	<i>sec</i> -Butyl alcohol	5	105
Trichloroethylene	90	<i>sec</i> -Butyl alcohol	10	95
Trichloroethylene	95	<i>tert</i> -Butyl alcohol	5	80
Trichloroethylene	90	<i>tert</i> -Butyl alcohol	10	70
Trichloroethylene	100			None
Ethylene dichloride	100			Below 60
Ethylene dichloride	90	Chloroform	10	65
Ethylene dichloride	70	Chloroform	30	90
Ethylene dichloride	60	Chloroform	40	None
Ethylene dichloride	90	Carbon tetrachloride	10	70
Ethylene dichloride	80	Carbon tetrachloride	20	80
Ethylene dichloride	70	Carbon tetrachloride	30	None
Ethylene dichloride	90	Trichloroethylene	10	55
Ethylene dichloride	60	Trichloroethylene	40	65
Ethylene dichloride	40	Trichloroethylene	60	95
Ethylene dichloride	80	Methylene chloride	20	60
Ethylene dichloride	65	Methylene chloride	35	70
Ethylene dichloride	60	Methylene chloride	40	None
Dichloroethylene	100			50
Chloroform	100			None
Carbon tetrachloride	100			None
Carbon tetrachloride	60	Acetone	40	Below 32
Carbon tetrachloride	70	Acetone	30	Below 32
Carbon tetrachloride	80	Acetone	20	57
Carbon tetrachloride	20	Toluene	80	57
Carbon tetrachloride	30	Toluene	70	74
Carbon tetrachloride	40	Toluene	60	Above 86

chlorinated products are required. This, of course, is not the only factor, since vapor pressure (boiling point), thermal stability, and other factors also enter. For instance, Ellis (33) has shown that solid chlorinated de-

rivatives dissolved even in large quantities in inflammable solvents will not appreciably reduce the inflammability of the latter.

In the case of the aliphatics, the amount of chlorine necessary to give a non-flashing product at ordinary temperature decreases with increase in boiling point. A rough approximation of the minimum requirement for

TABLE 5
Toxicity of chlorinated hydrocarbons

CHLORINATED HYDROCARBON	FORMULA	RELATIVE TOXICITY (CCl ₄ = 1)
Carbon tetrachloride.....	CCl ₄	1.0
Perchloroethylene.....	C ₂ Cl ₄	1.6
Trichloroethylene.....	C ₂ HCl ₃	1.7
Dichloroethylene.....	C ₂ H ₂ Cl ₂	1.7
Chloroform.....	CHCl ₃	2.2
Pentachloroethane.....	C ₂ HCl ₅	6.2
Tetrachloroethane.....	C ₂ H ₂ Cl ₄	9.1

TABLE 6
Toxicity of chlorinated hydrocarbons

CHLORINATED HYDROCARBON	FORMULA	RELATIVE TOXICITY
Ethyl chloride.....	C ₂ H ₅ Cl	1.0
Carbon tetrachloride.....	CCl ₄	3.0
Trichloroethane.....	CH ₃ CCl ₃	3.5
Ethylidene dichloride.....	CH ₃ CHCl ₂	4.3
Dichloromethane.....	CH ₂ Cl ₂	4.3
Trichloroethylene.....	CHCl:CCl ₂	5.6
Dichloroethylene.....	CHCl:CHCl	6.0
Chloroform.....	CHCl ₃	7.0
Dichloroethane.....	CH ₂ ClCH ₂ Cl	8.0
Tetrachloroethylene.....	CCl ₂ :CCl ₂	9.3
β-Trichloroethane.....	CH ₂ Cl·CHCl ₂	14.0
Tetrachloroethane (<i>sym</i>).....	CHCl ₂ ·CHCl ₂	16.0
Pentachloroethane.....	CHCl ₂ ·CCl ₃	18.7

non-inflammability at ordinary temperatures may be obtained from the following table:

<i>Series chlorinated</i>	<i>Per cent chlorine which must be substantially exceeded to prevent flashing</i>
Methane.....	90
Ethane.....	70
Pentane.....	53

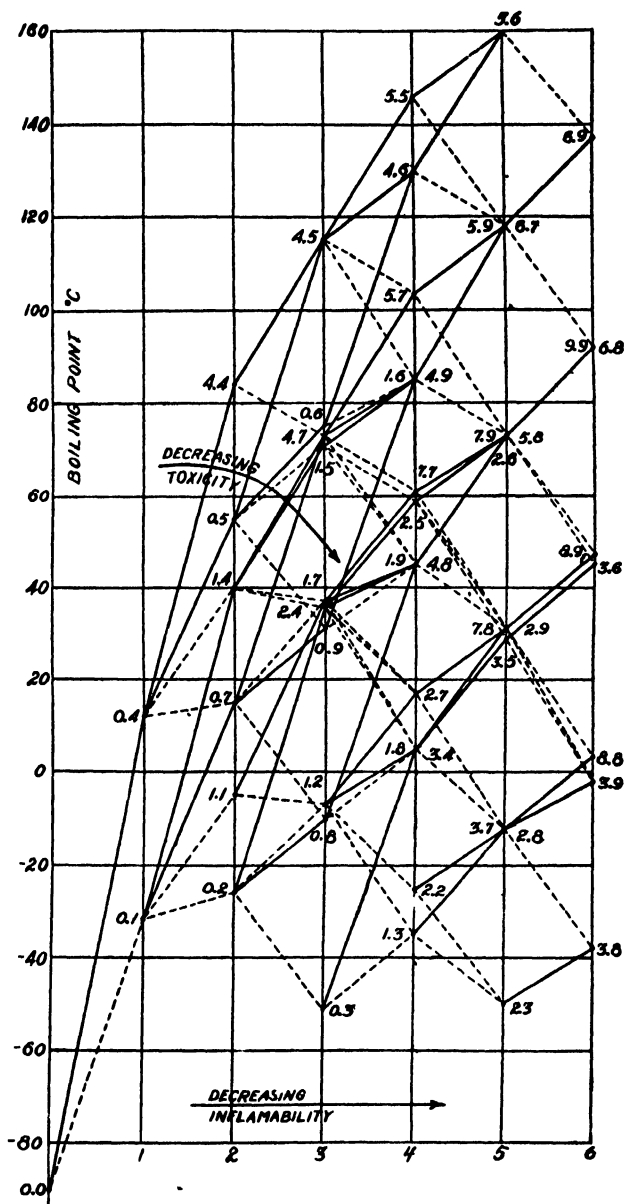


FIG. 1. Properties of fluoro-chlorinated hydrocarbons. 0 = CH₄; 1 = CH₃F; 2 = CHF₃; 3 = CF₄; 4 = CH₂Cl; 5 = CHCl₂; 6 = CCl₄; 7 = CHClF; 8 = CClF₂; 9 = CCl₂F.

Table 3 lists the ignitable concentrations of mixed solvents, while table 4 gives the flash points of such mixtures. It must be borne in mind that the inflammability of a mixture may vary with the amount and rate of solvent evaporated, depending on the vapor pressures of the components and other factors (66, 68).

Because of their higher boiling points, the butyl and amyl polychlorides offer possibilities in the solvent field, especially since a lower amount of chlorine is necessary to produce non-inflammable properties. Where high stability is not required, they should be available at a cheap price.

TOXICITY

One important property of these materials is toxicity. There does not seem to be any definite correlation between structure and toxicity, the relative toxicities being given by Henderson and Haggard as shown in table 5 (40). This relationship is somewhat modified by Lazarew (52a), who gives the values shown in table 6.

The fluorinated compounds possess the advantage of physiological inertness, which should make them well fitted for solvent uses from this viewpoint.

Figure 1, taken from U. S. patent 1,968,050 (55), illustrates the relative toxicity of chlorides and fluorides in two-carbon atom molecules. The base line indicates the number of atoms of halogen per molecule. By means of the key given, it is possible to locate the effect of the various substituents. For instance, compound 0.1 is $\text{CH}_3\text{CH}_2\text{F}$, compound 2.9 is $\text{CHF}_2\text{CCl}_2\text{F}$, and compound 2.2 is CHF_2CHF_2 . The dashed lines indicate fluorine substitutions, and the solid lines indicate chlorine substitutions. It will be seen that the substitution of fluorine for chlorine greatly reduces the toxicity and also reduces the boiling point.

The aromatic chlorinated derivatives are generally considered quite toxic. These might also be improved by fluorination.

REFERENCES

- (1) ALLEN: J. Soc. Chem. Ind. **49**, 275 (1930).
- (2) American Paint and Varnish Manufacturers Association, Circular 378 February, 1931.
- (3) ANON. Chem. Age **29**, 476 (1933).
- (4) ANON. Chem. Age **26**, 678 (1932).
- (5) ANON. Ind. Chemist **9**, 349, 448 (1933).
- (6) ANON. Chem. Trade J. **92**, 227 (1933).
- (7) ANON. Ind. Chemist **9**, 349, 448 (1933).
- (8) ANON. Chem. Markets **31**, 227 (1932).
- (9) AYRES Ind. Eng. Chem. **21**, 899 (1929).
- (10) AYRES U. S. patent 1,741,393, December 31, 1929.
- (11) BAHR AND ZIELER: Z. angew. Chem. **43**, 232 (1930).

- (11a) BALDESCHWIELER, TROELLER, AND MORGAN: *Ind. Eng. Chem., Anal. Ed.* **7**, 374 (1935).
- (12) BERL AND BITTER: *Ber.* **57**, 95 (1924).
- (13) BOOTH AND BIXBY: *Ind. Eng. Chem.* **24**, 637 (1932).
- (14) BORN: U. S. patent 1,944,859, January 23, 1924.
- (15) BROWN: *Ind. Eng. Chem.* **20**, 183 (1928).
- (16) BUC (Standard Oil Development Co.): U. S. patent 1,391,758, November 22, 1920.
- (17) BUC (Standard Oil Development Co.): U. S. patent 1,436,377, August 13, 1920.
- (18) CARLISLE AND COYLE: *Chem. Markets* **29**, 243 (1931).
- (19) CARLISLE AND LEVINE: *Ind. Eng. Chem.* **24**, 146, 1164 (1932).
- (19a) Chem. Fab. von Heyden: German patent 566,034, February 4, 1931.
- (20) CLARK: *Ind. Eng. Chem.* **22**, 439 (1930); *Chem. Met. Eng.* **38**, 206 (1931).
- (21) COFFIN AND MAASS: *Can. J. Research* **3**, 525 (1930).
- (22) COFFIN, SUTHERLAND, AND MAASS: *Can. J. Research* **2**, 267 (1930).
- (23) CURME: *Chem. Met. Eng.* **24**, 999 (1921).
- (23a) DASCHLAUER AND EGGERT: German patent 441,747, March 10, 1927.
- (23b) DICKINSON AND LEERMAKERS: *J. Am. Chem. Soc.* **54**, 3852 (1932).
- (23c) DIETRICH AND LOHRENGEL: *Z. angew. Chem.* **47**, 830 (1934).
- (23d) DOBRYANSKII ET AL.: *J. Applied Chem. U. S. S. R.* **6**, 1133 (1933); U. S. patent 1,950,720, March 13, 1934.
- (24) Dow Chemical Co.: U. S. patent 1,858,521, August 26, 1927.
- (25) Dow Chemical Co.: U. S. patent 1,841,279, December 26, 1928.
- (26) Dow Chemical Co.: U. S. patent 1,900,276, July 27, 1928.
- (26a) Dow Chemical Co.: U. S. patent 1,989,478, January 29, 1935.
- (27) Dow Chemical Co.: U. S. patent 1,971,318, August 21, 1934.
- (27a) Dow Chemical Co.: U. S. patent 2,018,345, October 22, 1935.
- (28) Dow Chemical Co.: U. S. patent 1,819,585, August 18, 1928; U. S. patent 1,917,073, July 4, 1933.
- (28a) Dow Chemical Co.: U. S. patent 1,946,040, February 6, 1934.
- (29) Dow Chemical Co.: U. S. patent 1,835,682, November 20, 1930.
- (30) Dow Chemical Co.: U. S. patent 1,938,714, December 12, 1933.
- (31) DURRANS: *Chem. Age* **29**, 605 (1933).
- (32) EGLOFF, SCHAAD, AND LOWRY: *Chem. Rev.* **8**, 1 (1931).
- (32a) E. I. du Pont de Nemours: U. S. patent 1,964,720, July 3, 1924.
- (33) ELLIS: Canadian patent 267,486, January 11, 1927.
- (34) ELLIS AND WELLS: U. S. patent 1,440,976, April 12, 1923.
- (35) ERNST AND WAHL: German patent 430,539, April 21, 1922.
- (36) FARRINGTON (Standard Oil Co. of California): U. S. patent 1,759,155, May 20, 1930.
- (37) FIFE AND REID: *Ind. Eng. Chem.* **22**, 513 (1933).
- (38) FROLICH AND WIEZEVICH: *Ind. Eng. Chem.* **24**, 13 (1932).
- (38a) Frigidaire Corp.: British patent 378,324, August 11, 1932.
- (39) HELLER: U. S. patent 1,851,970, June 26, 1930.
- (40) HENDERSON AND HAGGARD: *Noxious Gases*, American Chemical Society Monograph No. 35. The Chemical Catalog Co., Inc., New York (1927).
- (41) Holzverkohlung Industrie: German patent 393,550 (1924).
- (41a) I. G. Farbenindustrie: German patent 565,122, January 19, 1927.
- (42) I. G. Farbenindustrie: German patent 486,952, November 30, 1929.
- (42a) I. G. Farbenindustrie: German patent 518,166, May 9, 1924.

- (43) I. G. Farbenindustrie: British patent 283,119, January 3, 1928.
- (43a) I. G. Farbenindustrie: German patent 491,316, December 12, 1922.
- (44) I. G. Farbenindustrie: German patent 478,126, June 20, 1929.
- (44a) I. G. Farbenindustrie: U. S. patent 1,889,157, November 29, 1933.
- (45) I. G. Farbenindustrie: U. S. patent 1,944,306, January 23, 1934.
- (46) I. G. Farbenindustrie: U. S. patent 1,914,465, June 20, 1933.
- (47) I. G. Farbenindustrie: Canadian patent 301,674, July 1, 1930; French patent 674,254, January 27, 1930.
- (48) I. G. Farbenindustrie: U. S. patent 1,833,393, November 24, 1931; U. S. patent 1,833,358, September 10, 1928.
- (48a) Imperial Chemical Industries: British patent 378,866, August 16, 1932.
- (49) Imperial Chemical Industries: British patent 388,818, April 9, 1931.
- (50) JOHNS AND BUC (Standard Oil Development Co.): U. S. patent 1,440,683, March 11, 1921.
- (51) KHARASCH AND McNAB: J. Am. Chem. Soc. **56**, 1425 (1934).
- (52) KILLEFER: Ind. Eng. Chem. **19**, 636 (1927).
- (52a) LAZAREW: J. biol. méd. exptl. U. S. S. R. (Zhurnal eksperimentalnoi Biologii i Meditsiny) **12**, No. 33, 319-32 (1929); Leningrad, Gummiwerke, "Krasny j. Trengolnik," Chem. Zentr. **101**, I, 2762 (1932).
- (53) MAIER: French patent 655,930, April 25, 1929.
- (54) MAZE: U. S. patent 1,425,669, August 15, 1922.
- (55) MIDGLEY, HENNE, AND McNARY (General Motors Corp.): U. S. patent 1,968,050, July 31, 1934.
- (55a) Monsanto Chemical Co.: U. S. patent 1,935,648, November 21, 1933.
- (56) Naamlooze Venootschap Bataafsche Petroleum Maatschappij: British patent 338,742, January 14, 1931.
- (57) OTT AND PACKENDORFF: Ber. **64**, 1324 (1931).
- (57a) PADOVANI AND MAGALDI: Giorn. chim. ind. applicata **15**, 1-7 (1933).
- (58) PARK: Chemistry & Industry **50**, 620 (1931).
- (59) PIOTROWSKI AND WINKLER: J. Inst. Petroleum Tech. **17**, 225 (1931).
- (59a) Raschig G. M. B. H.: German patent 580,512, July 13, 1933 (addition to 575,765); U. S. patent 1,963,761, June 19, 1934.
- (60) Rhodes-Perry-Martin, Inc.: U. S. patent 1,940,688, December 26, 1933.
- (61) RICARD: U. S. patent 1,852,063, December 26, 1922.
- (62) Roessler and Hasslacher Chemical Co.: U. S. patent 1,816,895, August 4, 1931.
- (63) Roessler and Hasslacher Chemical Co.: Trichlorethylene, its Properties and Uses (1931).
- (64) Schering Kahlbaum: British patent 374,949, March 19, 1931.
- (64a) Shell Development Co.: Canadian patent 338,210, December 26, 1933.
- (65) SHERRILL: J. Am. Chem. Soc. **56**, 926 (1934).
- (66) SNELL: Ind. Eng. Chem. **22**, 893 (1930).
- (66a) Standard Oil Co. of Indiana: U. S. patent 2,017,568, October 15, 1935.
- (67) Standard Oil Co. of Indiana: U. S. patent 1,948,045, February 20, 1934.
- (67a) Standard Oil Co. of Indiana: U. S. patent 2,017,327, October 15, 1935.
- (68) Standard Oil Co. of Indiana: Canadian patent 324,181, June 13, 1931.
- (68a) Standard Oil Co. of Indiana: U. S. patent 2,031,144, February 18, 1936.
- (68b) Standard Oil Co. of Indiana: U. S. patent 2,031,145, February 18, 1936.
- (69) STOSACKER (Dow Chemical Co.): U. S. patent 1,754,656, April 15, 1930.
- (70) SUIDA (I. G.): German patent 485,434, October 31, 1929; U. S. patent 1,637,972, August 2, 1927.

- (70a) Texas Corp.: U. S. patent 2,022,616, November 26, 1935.
- (70b) THOMAS: Ind. Eng. Chem., News Ed. **12**, 100 (1934).
- (70c) TRAMM: U. S. patent 2,016,658, October 8, 1935.
- (71) VOESS: U. S. patent 1,921,054, August 8, 1933.
- (71a) WAHL: Compt. rend. **196**, 1900 (1933); **197**, 1330 (1933).
- (72) WEBB: U. S. patent 1,560,625, November 10, 1926.
- (72a) WERTYPORCH ET AL.: Ber. **66B**, 732 (1933).
- (72b) WHEELER: J. Indian Chem. Soc., Prafulla Chandra Ray Commemoration, **1933**, 53-60.
- (73) WIBAUT: Z. Elektrochem. **35**, 602 (1929).
- (74) WIBAUT, DREKMANN, AND RUTGERS: Proc. Acad. Sci. Amsterdam **27**, 671 (1924); Chem. Abstracts **19**, 1804.

THE PHYSICAL CHEMISTRY OF ASPHALTIC BITUMEN

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I. ORIGIN

Many theories have been advanced concerning the origin and methods of formation of petroleum and the naturally occurring asphaltic bitumens. The reader who is interested in the history and complete discussions of the various theories is referred to the works of Brannt (17), Peckham (75), and Redwood (82), with their numerous references to original sources. Redwood reviews very completely the inorganic, the terrestrial (plant) organic, and the marine organic theories concerning the origin of petroleum and related materials. He also summarizes very clearly the Engler-Höfer dual origin theory. Peckham expresses the opinion that asphaltic base oils are of animal origin, whereas paraffinic petroleums are derived from plant life.

One of the first papers concerning the inorganic origin of bitumen was written by the famous French chemist Berthelot in 1866. Mendeléeff in Russia was also an advocate of its inorganic origin and believed that simple hydrocarbons were formed by the action of water on metallic carbides. Later the simple gaseous hydrocarbons condensed and polymerized to form petroleum, which in turn probably was the forerunner of the naturally occurring bitumens. Both of these men argued that petroleum could not be of organic origin because carbon was not found associated with it.

Coquand advocated the theory that bitumens were formed by the condensation of marsh gas, while Hunt, Orton, and Lesley held the view that

bitumen is indigenous to the strata in which it is found. Maberry (50) believed in its organic origin and thought that the decomposition had taken place *in situ*, whereas Newberry, Peckham, and others argued that bitumen is a product of distillation and secondary decomposition of organic material.

Modern knowledge (19) concerning the nature of the hydrocarbons found in petroleum and the geological conditions (e.g., low temperatures) under which they are found are decidedly in favor of the organic origin. Some investigators ascribe the large number of different hydrocarbon compounds found in petroleum and asphalt to the anaerobic degradation of organic materials, both plant and animal, buried under heavy layers of sediment. Macfarlane (51) believes that fish were the chief source of material from which these complex hydrocarbons were derived, while others (40) consider that many types of animal and plant life, such as mollusks, diatoms, algae, protozoa, etc., may have been the original source. Treibs (112) discussed the probability of the production of petroleum from materials containing chlorophyll, and the experiments of Zelinskii and Koslov (123) indicated phytosterol and abietic acid as the possible sources of the optically active constituents. Also, humus acids and associated organic compounds have been considered (80) as the intermediate products between complex plant compounds and petroleum hydrocarbons.

Certain experiments (102) point to the possible formation of asphalt by the action of microorganisms on crude petroleum, while others (64) indicate that asphalt-like materials may be obtained by heating a mixture of gelatin and casein with hydrogen under pressure in the presence of calcium carbonate and magnesium carbonate. Hackford (39) studied the conversion of algae into bitumen by acid hydrolysis, and Friedman (33) concluded that asphaltic compounds were formed by reactions between olefins and sulfur. Similar products were not obtained when paraffin hydrocarbons were used. Chernozhukov (21) decided that the high molecular weight compounds (asphaltenes) in asphaltic bitumen are formed from petroleum by sulfur compounds of unknown composition. At high temperatures the radicals CH_3 , CH_2 , and CH may be stable (58), but on cooling they polymerize to form the hydrocarbons found in asphalt. The conditions under which the polymerization and condensation of petroleum to asphalt may take place have been discussed by Zalogiechi and Zielenski (122).

Richardson (86, 87) proposed the theory that the bitumen in Trinidad native lake asphalt was produced from petroleum by the surface action of colloidal clay. He further believed that the petroleum was produced from gaseous hydrocarbons by the catalytic action of the mineral bodies with which they came in contact. Tycinin (113) held essentially the same theory. He believed that, as petroleum rises to the surface of the earth,

certain constituents are coagulated by the sunlight and then deposited on soil particles. The more volatile portions of the oil are evaporated, and the heavier, less volatile compounds remain associated with the coagulated asphalt.

Vanadium (72, 70, 49) is frequently a constituent of the ash from asphaltic bitumens. Its occurrence leads to the belief (15) that the catalytic action of this metal may have had a prominent part in the formation of the hard asphalts from softer hydrocarbons.

II. NATURE OF THE HYDROCARBONS PRESENT

Although a large amount of work has been done to obtain data concerning the chemical constitution of petroleum hydrocarbons, very little information is available concerning the nature of the numerous complex compounds present in asphaltic bitumen. Richardson (85) mentions the series of polymethylenes which, when first found in Russian petroleum, were given the generic name of naphthenes. These compounds are not

TABLE 1
Molecular weights of bitumens

SOURCE OF BITUMEN	MOLECULAR WEIGHT
Trinidad lake asphalt.....	1132
Bermudez lake asphalt.....	620
Gilsonite.....	4252

as stable as paraffinic hydrocarbons and yet are not acted upon by sulfuric acid. By substitution of various hydrocarbon radicals for hydrogen, the polymethylenes may become very complex. Comparisons of synthetic polycyclic polymethylenes from California and Louisiana petroleum and from Trinidad lake asphalt have led to the conclusion that the asphaltic compounds of low boiling point may be bicyclic or bridge compounds, while those of high boiling point are polycyclic hydrocarbons.

Relatively small amounts of substituted hydrocarbons of the aromatic series may be found in the more volatile fractions of asphalt-base petroleum.

Strieter (101) dissolved asphaltic bitumen in benzene and determined the molecular weight by the lowering of the freezing point. Table 1 gives the values he obtained for three naturally occurring bitumens.

Katz (45), in a study of the effect of air-blowing on the chemical composition of a series of Alberta bitumens, found molecular weights for fractions of the original bitumen which ranged from about 750 to 2200. Treatment with air, which he believed caused condensation followed by

polymerization, resulted in increases in molecular weights up to almost 4700.

If the data of Strieter and Katz are taken as even approximate criteria, the compounds composing asphaltic bitumens must be very complex. The presence in asphalts of compounds containing sulfur, nitrogen, and occasionally oxygen makes even more difficult any attempt to separate and isolate individual compounds.

The saponification of mixtures of asphalt and drying oils was studied by Demarest and Rieman (25), using a potentiometric method. Previously Paillar (73) had developed titration methods for determining both the acid and saponification values for asphalts. Pöll (78) investigated the determination of the iodine number of native and oil asphalts and discussed the value of the number in determining the constitution of bitumen.

III. ACTION OF ORGANIC SOLVENTS

Fractional solution and precipitation by means of organic solvents has been used extensively in the analysis and testing of asphaltic bitumens. By this means the type and source of the asphalt frequently may be determined. Also the presence of added material, which may detract from the practical value of the original asphalt, may often be detected by the judicious use of partial solvents.

Although carbon disulfide and chloroform are two of the best solvents for asphaltic bitumens, Abraham (1) points out that caution should be exercised in using 100 per cent solubility in these liquids as a definition for bitumen.

Richardson and Forrest (84) found that bitumen, which was completely soluble in carbon disulfide, upon being treated with carbon tetrachloride frequently gave a residue or precipitate. These substances, insoluble in carbon tetrachloride but soluble in carbon disulfide, they called "carbenes." If the carbon tetrachloride solution of bitumen was permitted to stand for some time in a glass container exposed to sunlight the carbenes were increased in amount (3, 54). That the reaction producing these increased amounts of carbenes is a photochemical one is indicated by the fact that hydrogen chloride is formed and may be detected in the air above the solution. Further, light of short wave length is more effective in producing increased precipitation than is that of longer wave length. No increase in amount of precipitate will occur over a considerable length of time in the dark.

Light petroleum naphtha (86° or 88° Baumé) is another solvent commonly used to fractionate asphaltic bitumen. The usual proportions are 100 volumes of the naphtha to 1 volume of the bitumen. The soft, light-colored, low molecular weight constituents of the asphalt, which dissolve in the naphtha, are called "malthenes" or "petrolenes", whereas the hard,

dark-colored precipitate made up of high molecular weight compounds possessing a high carbon to hydrogen ratio is referred to as the "asphaltenes."

Associated with the petrolenes are the asphaltic resins, which may be separated from the non-resinous portion by mixing with fuller's earth, which adsorbs the resins. The petrolenes may be washed out of the mass by means of 86° B \acute{e} . naphtha and the resins then, at least partially, recovered from the surface of the fuller's earth by treatment with carbon disulfide, chloroform, or benzene. When removed from the surface of the fuller's earth the resins again become completely soluble in naphtha.

Oliensis (71) has proposed a test for determining the degree of homogeneity of asphalts in which the asphalts are dissolved or dispersed in 5.1 times their volume of a petroleum naphtha of specified properties. A drop of the dispersion placed on an inclined clean glass plate will give a smooth, clear, glassy film if the asphalt is homogeneous and a dull, matte-like streak in the center of the stain if it is not. The name "carboids" was suggested for the substances which are precipitated or are insoluble in the solvent. Naturally the presence of mineral matter in the bitumen complicates the test.

Nellensteyn (63) found that asphaltenes which are usually in a dispersed condition go into solution if a diluent is added which is completely miscible with both the dispersing medium (the petrolenes) and the protective agent (the resins). The added liquid (diluent) should have a surface tension greater than 24 to 26 dynes per centimeter at 25°C.

A method has been proposed by Schwarz (96) for classifying bitumen. The asphalts are etched by means of benzine, carbon tetrachloride, or carbon disulfide for 5 seconds and photomicrographs are taken of the surfaces. Bitumens of various types and sources presumably give different patterns and designs under the standardized treatment.

Recently Zwergal (124) extracted asphaltic bitumens successively with methyl, ethyl, propyl, butyl, and amyl alcohols. He found that the proportion of each fraction varied with the bitumen, and that the third fraction (extracted with propyl alcohol) had a higher carbon and hydrogen content than the other fractions, owing to the small quantity of sulfur and oxygen present. This fraction also possessed the highest ductility.

The refining and fractionation of petroleum by means of solvents (46) has developed very rapidly in recent years. Although these processes are frequently concerned with the reactions of asphaltic bitumen (18), they are too involved to be discussed here.

IV. COLLOIDAL PROPERTIES

Many of the characteristics of asphaltic bitumen indicate that they are colloids; some of these properties and the theories concerning structure

will be briefly discussed. Nellensteyn (59, 61) has argued that asphalts are colloids because their solutions exhibit the Tyndall effect even at dilutions of 1 to 30,000, and because ultramicroscopic examination shows perceptible Brownian movement in the solution. He reports that ultramicroscopic particles were detected (60) in solutions of both native and oil asphalts. However, in the case of the former these may have been very small mineral particles which are practically impossible to remove by even the finest filters (85). From his researches Nellensteyn has developed a theory for the colloidal structure of asphaltic bitumen which is based upon the existence of three components. They are (1) the fluid medium or dispersing phase, (2) the protective bodies which are lyophilic, and (3) a lyophobic part. The micelles of the dispersed phase are composed of the last two groups, and the stability of the system is dependent upon the interfacial forces existing between the fluid medium and the micelles. When an asphalt solution is flocculated by the addition of some organic solvent a new phase is not formed; the dispersed particles merely come together because of the change in interfacial tension which has taken place between them and the surrounding liquid. The theory assumes that elementary carbon is at the center of each micelle and, in fact, Waterman and Nellensteyn (117) claimed to have obtained carbon from artificial and natural asphalts by successive extractions with gasoline, carbon tetrachloride, and benzene. The presence of free carbon is also suggested by the dark color of the asphalt. "Most hydrocarbons are only slightly colored; the same could be expected of the colloidal solutions, even of the highly polymerized ones. The dark color of asphalt solutions therefore indicates the presence of free carbon." The micelles may be pictured as composed of successive layers of hydrocarbons in which the ratio of carbon to hydrogen becomes less as progress is made away from the center or carbon nucleus. This ratio for the outer layer of the micelles will be very nearly the same as for the dispersing phase (petrolenes).

Asphaltic bitumens are strongly adsorbed by certain types of mineral surface. By drawing asphaltic base petroleum upward through a column of dry fuller's earth, Gilpin and Schneeberger (35) obtained fractions practically free of colored material and possessing specific gravities much lower than the original petroleum. They concluded that asphaltic petroleum is an emulsoid, and that passage through a column of fuller's earth causes the adsorption and coagulation of the bitumens present, which in turn carry with them the sulfur and nitrogen compounds and the aromatic and olefinic hydrocarbons.

Guiselin and Handricourt (38) also found that the filtration of petroleum through dried earth produces a series of fractions, the first of which are water-white and possess a faint ethereal odor. Those hydrocarbons richest in carbon are the most attracted by clay.

The adsorption of asphalt from carbon disulfide solution by crushed granite, feldspar, and quartz was investigated by Dow (26). He used changes in the color of the dilute (0.5 per cent) solutions employed as a measure of the amount of adsorption. The coloring matter removed from petroleum by clay is believed by Bosshard and Wildi (16) to be colloidal in nature.

Zaharia and Lucatu (121) subjected several petroleums to ultrafiltration in an effort to determine whether the paraffins, resins, and asphalts were present in colloidal or true solution. They employed vulcanized rubber membranes (0.04 mm. thick) in the Bruckner apparatus, under a pressure of 150 atmospheres. The "resins," which are separated from the petroleum by means of 70 per cent ethyl alcohol, and the paraffins were found to be ultrafiltrable. Both hard and soft asphalts were removed quantitatively by ultrafiltration. Thus it was concluded that the asphaltic bodies present in petroleum are colloidal, but that the resins and paraffins are in true solution. The retained asphalts, dissolved in benzene and cyclohexane, were subjected to ultrafiltration, but they would not pass through the rubber membrane.

Pyridine is an excellent solvent for asphaltic bitumen. Since the author had used rubber membranes and pyridine in the study of other systems (103, 105), he applied this combination of membrane and solvent to a study of various bitumens. Cells equipped with membranes of dentist's rubber dam were filled with 5 per cent solutions of various hard asphalts in pyridine, and the under side of the membrane brought into contact with c.p. pyridine. The contents of the cells were agitated in order that a fresh layer of solution would be continuously presented to the semipermeable membrane. It should be noted that dialysis through a rubber membrane depends upon the solubility of the material in the rubber; in this respect it differs from the sieve-like action of some membranes. The pyridine outside of the cell became colored by the asphaltic materials passing the membrane. The outer liquid was changed from time to time, because as the concentration of the asphaltic materials increased therein the rate of transfer through the membrane became slower. After twenty-one days the dialysis was stopped. The pyridine was allowed to evaporate spontaneously from the combined diffusates and from the dialyzate, the latter having been washed out of the cell with pure pyridine. The residues from the diffusate and dialyzate were weighed, and their combined weight subtracted from the total bitumen used in order to obtain the amount of volatile hydrocarbons lost from the diffusate along with the pyridine.

Table 2 gives the weight per cents of the original asphalt recovered from the pyridine solutions and the loss, which probably is mainly volatile hydrocarbons lost during the evaporation (at room temperature) of the pyridine from the diffusate.

The dialyzates from all four kinds of asphalt were black, hard, and brittle. However, the characteristics of the diffusates from different bitumens may vary considerably, although the quantities obtained from a given amount of original material may be nearly the same. Examination of the results of the dialysis of solutions of various types of bitumen should be very helpful in solving the complex problems encountered in a study of the physical structure of asphaltic bitumens.

Mack (53) considers that at low temperatures asphalts are sols of asphaltenes in a mixture of resins and petrolenes. However, as the temperature is raised solution occurs; for the asphalts studied the process is complete at 120°C., and the liquids acquire the characteristics of true solutions.

TABLE 2
Fractionation of asphalts by dialysis

TYPE OF BITUMEN	WEIGHT PER CENT OF		
	Dialyzate	Diffusate	Loss
Trinidad batch steam-refined oil asphalt (10 penetration at 77°F., 100 g./5 sec.)	55	27*	18
Venezuelan batch steam-refined oil asphalt (10 penetration)	54	27†	19
Venezuelan air-blown asphalt (10 penetration)	58	22‡	20
Bitumen from Trinidad refined lake asphalt (7 penetration)	72	18*	10

* Comparatively hard. Tacky.

† Comparatively soft. Tacky but long.

‡ Comparatively very soft. Oily, slightly tacky, short. Lighter colored than the others.

The molecular weights of the asphaltenes were calculated from the concentration and viscosity of solutions in petrolenes and benzene by means of the equation,

$$\log \text{ relative viscosity} = ckM \quad (1)$$

(where c = concentration in weight per cent, M = molecular weight, and k = a constant) and were found to be of the order of 1800. These determinations, together with the measurements of adsorption of asphaltic resins by asphaltenes, indicate that the high viscosities of asphalt are caused by association and not by solvation.

Bateman and his coworkers (10, 11) have studied the effect on asphalts

of mixing them with sand and stone at elevated temperatures. Improvements (2) in the method of recovery of bitumen from mixtures with mineral aggregate have made investigations similar to those of Bateman much more valuable and reliable. There are many indications that different types and kinds of bitumen are affected to different extents by contact with hot sand and stone, especially in the presence of air. Recently, Sikes and Corey (99) studied experimentally the effect of continued heating on various kinds of asphalt. The fact that asphalts at atmospheric temperatures frequently possess anomalous flow properties has been taken by Traxler and Coombs (109) as evidence of the colloidal nature of bitumens.

V. OPTICAL PROPERTIES

Engler and Steinkopf (27) found the quantity of optically active material in petroleum to be so small that numerous fractionations had to be made to obtain a sufficient concentration for accurate study. They obtained evidence that the activity was due to decomposition products of cholesterol, and that overheating caused a diminution of activity either by racemization or by complete deactivation. Every petroleum studied by them showed some optical activity. Rakuzin (81) had detected cholesterol itself in petroleum, but later investigations (100), using the digitonin reaction on Java and Mendoza oils, made it appear doubtful that the free compound exists in petroleum. Marcusson (56), also, is of the opinion that the optical activity of mineral oils is due to saturated hydrocarbons formed from cholesterol or its compounds.

Solutions of untreated and sulfonated asphalts in benzene, chloroform, and hydrocarbon solvents were prepared by Rosinger (90). The solutions were poured out on glass plates and the solvent allowed to evaporate, leaving thin films of the asphalt. When these films were exposed to light, changes, probably due to oxidation, occurred in the bitumen which rendered it insoluble in the solvent used in preparing the original solution.

At about the same time Gödrich (36) found that the action of light on asphalt made it more insoluble in the usual solvents. Further, the sensitivity of the asphalt to light was increased by the presence of sulfur monochloride. Although Gödrich found that solutions of asphalt showed absorption bands in the blue and yellow, some of our own unpublished studies have shown the complete absence of absorption bands either in the visible or ultra-violet transmission or reflection spectra. In asphalts containing sulfur Gödrich found the absorption bands in the yellow to be missing. According to him, asphalt is sensitive to monochromatic light over the entire range of the visible spectrum as well as into the ultra-violet.

Bitumens exposed to air and sunlight were found by Reeve and Lewis (83) to undergo changes other than those due to loss of volatile matter.

These investigators came to the conclusion that polymerization and intermolecular reactions induced by heat and possibly by light were largely responsible for these changes.

Errera (28) has discussed the early work of Kayser (1879), who isolated three components of asphalt by dissolving successively in alcohol, ether, and chloroform. Kayser called the three fractions α -, β -, and γ -asphalt. Alpha asphalt is an oily substance, while beta asphalt is a gummy solid with a softening point of about 60°C. Gamma asphalt, the only one of the three which is really sensitive to light, is high in sulfur content and melts at about 165°C. According to Errera, Judæan and Trinidad asphalt contain 58 and 38 per cent, respectively, of gamma asphalt. This component, which roughly corresponds to the asphaltenes mentioned above, is chiefly in a colloidal state.

During an investigation of asphalts from the region of the Black Sea, Tycinin (113) found that an ether extract which was free from asphalt continued to deposit material on standing. In darkness the deposition stopped, and then started again on exposure to light. Large surfaces of nickel, glass, and other solids increased the amount of deposit. Tycinin believed the change was not a chemical reaction but only a transformation of material into another physical state. These changes are somewhat analogous to the formation of "carbenes" in carbon tetrachloride solutions of asphalt exposed to sunlight.

Macht (52) found that thin films of asphalt on glass plates gave a greenish-yellow fluorescence under ultra-violet light, and that the color of the fluorescence deepened as the asphalt became harder. Films of coal tar gave a dark brown fluorescence. Benzene and benzine solutions of asphalts from various sources showed different colors under ultra-violet light. Mixtures of tar and asphalt were tested by placing a few drops of a benzene solution of the mixture on filter paper and permitting the solvent to evaporate before irradiation. Macht claims that with practice an accuracy of 5 per cent in estimating the proportions of asphalt and tar may be attained. Bruckner and Meinhard (20) also found that petroleum pitch, coal-tar pitch, and montan wax, either in solid form or in solution in carbon tetrachloride, chloroform, benzene, or petroleum naphtha, could be identified by their fluorescence in ultra-violet light. However, they claim that one material cannot be identified when mixed with others.

Hradil (42) has examined the fluorescence of oil shales spectroscopically, and Bentz and Strobel (13) report that crude oil can be distinguished from the refined product by the fluorescence shown under ultra-violet light.

In the opinion of Schwarz (97) the refractivity of individual hydrocarbons is a source of information which has not been completely utilized in the past. He also believes that etching with benzene, carbon tetrachloride,

carbon disulfide, and other solvents, followed by microscopic examination of the etched surfaces, may lead to valuable information concerning the proportions of resins, asphaltenes, carbenes, and carboids in an asphalt.

Although the Raman effect has not been studied in connection with asphaltic bitumen, Hibben (41) has discussed the applications and limitations of Raman spectra in the petroleum industry and has given data on cracked and uncracked gasolines and oils.

The colors of particular asphalts are of practical interest, especially when the bitumens are to be compounded with pigments. A Klett colorimeter has been used by the writer and his associates to estimate the color of bitumens obtained from various sources and by different methods of preparation. Although only comparative data are available at the present time, a procedure somewhat similar to the optical density method described by Ferris and McIlvain (29) for assigning numerical values to lubricating oils might be devised. Graefe (37) compared very dilute solutions of asphalt in benzene (1 to 10,000 parts) with an aqueous solution composed of 0.1 per cent iodine in a 0.2 per cent solution of potassium iodide. He found air-blown asphalts to be the darkest in color, while natural asphalts were the lightest.

VI. SURFACE TENSION

Measurement of the surface tension of asphaltic bitumens is very difficult, because at ordinary temperatures most of them are not fluid in the ordinary sense of the term. Only by making the measurements at elevated temperatures has it been possible to obtain estimates of the interfacial tension between air and asphalts of the consistencies usually employed industrially or in paving.

Surface tensions were determined for (1) Venezuelan crude oil of specific gravity 0.9509 at 60°F., (2) Trinidad petroleum of specific gravity 0.9497 at 60°F., and (3) a petroleum from the Island of Trinidad with a specific gravity of 0.9176. Table 3 gives the values obtained on these three asphaltic base petroleum at various temperatures by means of the duNoüy ring method.

The Venezuelan petroleum was saturated with water (an emulsion with water as internal phase was formed) and the surface tension measured at 28°C. by means of the duNoüy instrument. The value obtained was 33.0 dynes per centimeter, which is about the same as for the unsaturated oil. Distilled water was then agitated with about one-tenth of its volume of Venezuelan oil, allowed to stand overnight, and then separated from the petroleum. The oil-saturated water was found to have a surface tension of 58 instead of 72 dynes per centimeter. Thus, there is a difference in surface tension of 25 dynes per centimeter between Venezuelan oil saturated

with water and water saturated with oil. This value represents the force which is working toward the production of an emulsion with water as internal phase in such a system. It is this force which must be overcome in producing bituminous emulsions with water as external phase from this asphalt.

When similar experiments were performed using the Trinidad petroleum, which had the same specific gravity as the Venezuelan, the difference between the surface tensions of oil saturated with water and water saturated with oil was found to be only 20.5 dynes per centimeter. Therefore, less force has to be overcome in preparing an external phase emulsion using this petroleum or bitumens derived from it by distillation than when the Venezuelan oil or its derivatives are used. Practical experience in the production of commercial bituminous emulsions has confirmed this conclusion.

TABLE 3
Surface tension of asphaltic petroleum

PETROLEUM	TEMPERATURE	SURFACE TENSION
	°C.	dynes/cm.
Venezuelan	26	34.5
	56	30.0
	84	27.0
Heavy Trinidad	25	34.0
	55	32.5
	85	30.5
Light Trinidad	26	28.5
	58	26.0
	83	25.0

A soft asphaltic bitumen (48 seconds float (6) at 150°F.) prepared by steam distillation of petroleum from the Island of Trinidad was agitated slowly at 85°C. with 0.01 *N* sodium hydroxide and then allowed to stand until the temperature dropped to 25°C. The asphalt was skimmed from the surface of the solution, which was dark brown in color. The original 0.01 *N* sodium hydroxide had a surface tension of 59 dynes per centimeter, whereas the above-mentioned solution gave 35 dynes per centimeter, a drop of 24 dynes per centimeter. This decrease in surface tension was due to the formation of dark-colored, soap-like substances by the interaction of the sodium hydroxide and substances present in the bitumen. These soap-like compounds, upon isolation, were found to be excellent emulsifying agents for bitumens which otherwise were rather difficult to emulsify.

Emulsions with water as external phase, prepared from the soft Trinidad residuum and 0.01 *N* sodium hydroxide, gave surface-tension values of 33 dynes per centimeter. Since this figure is almost identical with that obtained on the solution mentioned above, it may be concluded that the continuous phase of the emulsion is very similar to the soap-like solution prepared by careful extraction of the bitumen with a solution of caustic soda.

Some measurements of the surface tensions of petroleums were attempted using glass capillary tubes, but the results were unsatisfactory, probably because of adsorption at the glass wall.

Francis and Bennett (31) used the duNoüy ring apparatus to measure the surface tensions of various domestic crude petroleums, and obtained values ranging from 29.0 to 31.2 dynes per centimeter at 85°C.

Using Jaeger's (43) method, Nellensteyn and Roodenburg (62) measured the surface tensions of the following asphalts at temperatures ranging from about 100° to 225°C.

- (1) Oxidized Venezuelan asphalt. (Ring and Ball softening point = 64.2°C.).
- (2) Mexican asphalts. (Ring and Ball softening points = 42°, 55.7°, and 58.5°C.).
- (3) Bitumen from Trinidad native lake asphalt. (Ring and Ball softening point = 65°C.).

The surface tensions of a coal-tar pitch (Ring and Ball softening point = 60.2°C.) were determined at temperatures ranging from 67° to 180°C.

They found that the surface tensions of the asphalts all fell within the limits 20.7 to 37.4 dynes per centimeter. Also, all of the temperature surface tension curves showed a sharp break at about 150°C. Nellensteyn and Roodenburg discussed the theoretical and practical significance of this break, and attributed it to sudden changes in the internal structure of the bitumen.

They also extracted the oily medium (petrolenes) from the various bitumens by means of naphtha and acetone, and then obtained surface-tension data on the recovered, solvent-free, bituminous fractions. For these fractions the temperature range was much greater (30° to 230°C.) than for the asphalt itself, because the petrolenes are fluid at the lower temperatures. A break also occurred in the surface tension-temperature curve for the petrolenes, but at a temperature of about 50°C.

Saal (95) was unable to verify the results obtained by Nellensteyn and Roodenburg, although, using the duNoüy method, he investigated several asphalts of different origins and methods of processing. He concluded that the breaks in the temperature-surface tension curves found by the previous investigators were due to experimental errors caused by using Jaeger's

bubble method to measure the surface tension of materials possessing viscosities above 15 poises. Consequently, Saal believes that Nellensteyn's conclusions concerning the internal structure of asphaltic bitumen at temperatures below the break in the curve are unjustified.

Nellensteyn and Roodenburg explain the greater miscibility of Trinidad asphalt with tar as being caused by its having a slightly higher surface tension than that possessed by most other asphaltic bitumens. When the surface tension of an asphalt is determined, it is probably the continuous phase (petrolenes) which is evaluated, since the micelles (asphaltenes) should have very little effect.

VII. INTERFACIAL TENSION BETWEEN ASPHALTIC BITUMENS AND WATER OR AQUEOUS SOLUTIONS

The formation of emulsions, in which water is the internal phase, with crude oils is of rather common occurrence, and the breaking of these oil-field emulsions is often a serious problem involving large expenditures of time and money. On the other hand, the production of bituminous emulsion, in which the asphalt is dispersed in the form of very small drops in a continuous phase usually composed of an aqueous soap solution or a very dilute clay slurry, has grown to be a business of large proportions. In both of these types of emulsion the tension which exists at the oil-water or oil-aqueous solution interface is an important property. As in determining the surface tension of bitumens, it is difficult to measure the interfacial tension between water and a hard bitumen which does not flow easily at ordinary temperatures.

Moreover, the interfacial tension must be determined at temperatures below the boiling point of the aqueous solution. Thus, a limitation is encountered immediately which does not appear in the evaluation of surface tension.

By forming drops of water in oil Johansen (44) studied the interfacial tensions developed between water and various light-colored petroleum products. The drops were counted and their total volume measured at the end of the experiment, and thus the average drop size was determined. Because of their dark color and opacity asphaltic materials could not be used as were the oils in Johansen's experiments. However, the author tried to measure the interfacial tension between soft asphaltic bitumen and water or alkaline solutions by forming drops of the bitumen in the aqueous medium. The experiments were not successful, chiefly because the water wetted the tip of the glass capillary better than did the bitumen, and because there was very little difference in density between the water or aqueous solution and the soft bitumens which were employed.

Weiss and Vellinger (119), and Vellinger (115) studied the influence of

temperature, pH, and degree of refining of petroleum oils on the interfacial tensions which they develop against water.

Using the duNoüy ring tensiometer, Traxler and Pittman (104) measured, at 85°C., the interfacial tension between various concentrations of sodium hydroxide solution and two soft asphaltic bitumens. The bitumens used were prepared from Venezuelan and Trinidad petroleum by steam distillation and had specific gravities at 85°/85°C. of 0.9964 and 0.9970, and floats at 150°F. of 44 and 53 seconds, respectively. It was found that the addition of sodium chloride up to a concentration of 0.125 *M* reduced the interfacial tension, whereas greater concentrations of salt increased the tension. The presence of calcium chloride up to a concentration of 0.0025 *M* in the aqueous phase increased the interfacial tension, but beyond that figure the tension values remained constant. The influence of calcium chloride could be partially counteracted by the addition of sodium chloride; at ratios which varied from 50 to 100 parts of sodium chloride to one of calcium chloride the salts completely neutralized the effect of each other.

The same bitumens were later used (104) in experiments to determine the interfacial tension against dilute solutions of disodium hydrogen phosphate, sodium tetraborate, sodium carbonate, sodium silicate, and sodium phosphate. At 85°C. solutions of sodium silicate and sodium phosphate gave lower interfacial tensions than disodium hydrogen phosphate and sodium tetraborate. Solutions of sodium carbonate were found to give values intermediate to these two groups. Further, the nature of the anion present in the aqueous solution was found to have more influence than the pH on the interfacial tension.

Nellensteyn and Roodenburg (65), from a study of the spreading of water on asphaltic bitumens and tar, concluded that Antonov's rule applied to such systems. This rule states that the tension at an interface equals the difference in surface tensions of the two liquids. However, this relation holds only for pure liquids which are immiscible. Since water does dissolve some material from most bitumens, adherence to Antonov's rule would not be expected. Experiments conducted by the writer and his colleagues indicated that such a conclusion is correct.

VIII. ADHESION OF BITUMENS TO SOLID SURFACES

The ability of bitumens to wet and adhere to solid surfaces is of practical value in the application of asphalts to paving, waterproofing, impregnation of felts, fabrics and fibres, as binders, paints, etc. Bain (7) emphasized the necessity of proper wetting of the solid surfaces by bitumen in most of its uses, and pointed out that in the native asphalts nature has accomplished almost perfect wetting of the dispersed mineral by the bitumen.

Bartell and Miller (8) studied quantitatively the wetting of silica by various petroleum, and obtained displacement pressures which varied from about 109 to 259 g. per square centimeter. Later these same investigators (9) measured the displacement of crude oil from silica by aqueous solutions. The solutions which were most reactive toward silica displaced the petroleum most readily.

An apparatus for measuring the adhesive properties of bituminous pipe-coating compounds has been described by Christopher (22). The mechanism and theory of the wetting of solids by liquids has been presented by McLean and Kohman (55) and by Peek and McLean (74). Nellensteyn (66) reviewed the energy relations existing between bitumens and solid materials. Fricke and Meyring (32) determined the wetting power of asphalt and tar and mixtures of them for glass by measurement of the angle of contact which the materials make with a clean surface.

Recently, Lee (48) has studied the displacement of tar and bitumen films from various solid surfaces by means of water. He gives a clear, concise exposition of the use of contact angles for measuring the wetting of a solid by a liquid.

It has been proposed (120, 47), that the characteristics of bitumen-mineral mixtures are greatly influenced by the surface forces acting between the solid and liquid. Wedmore (118), during an evaluation of materials for the exclusion of water in electrical apparatus, devised a method by means of which the adhesiveness of bituminous compounds may be measured. A cylindrical steel mold filled with the material being tested rests on a very highly polished steel plate. The plate and mold are slowly pulled apart at 20°C. A satisfactory material is arbitrarily classified as one which adheres to at least 90 per cent of the exposed surface.

Saal (91) believes that the adhesion of bitumens to solids is to a great extent influenced by the surface condition of the solid. Riedel and Weber (88), also, have expressed the opinion that the properties of the stone have a greater influence on the adhesiveness in a paving mixture than do those of the bitumen. The presence of soaps and electrolytes has a definite effect on the adhesiveness between stone and bitumen, consequently the adhesiveness of hot bitumen to various stones is less variable than is that of bituminous emulsions. Dahlberg (24) objected to the work of Riedel and Weber, because it was all done at 100°C., and made the suggestion that values be obtained for adhesion at 100°, 70°, 50°, and -10°C. Nüssel and Neuman (69) test for adhesion of bitumen to stone by boiling the coated solid with solutions of sodium carbonate. Their results do not agree with those obtained by the method proposed by Riedel and Weber. Although it is rather difficult to prove, the belief is held by most investigators that the adhesion of bitumen to stone increases with time.

The presence of small amounts of paraffin wax has been shown by Riehlm (89) to decrease the adhesiveness of asphaltic bitumens greatly, and he established 2.5 per cent of paraffin wax as the maximum permissible content if good adhesion is to be obtained.

The slipperiness of asphalt surfaces, a property of considerable practical importance, has been discussed by Nellensteyn (67) as a problem in the surface wetting of bitumen by water. In his opinion, an extensive knowledge of the surface and interfacial tensions of the materials involved appears to be essential to an understanding of the subject of slipperiness.

IX. FLOW PROPERTIES

Of the numerous empirical methods used for measuring the consistency of asphalts and similar materials one of the most widely used is the penetration test (4). The penetrometer measures the distance a needle of definite shape will enter the material when a standard load is applied at a standard temperature. Various methods have been developed for determining the so-called softening point, which is simply the temperature at which the material under test attains a certain consistency. The consistency of asphalts at the temperatures known as their Ring and Ball softening points (5) has been reported (30) to be about 12,000 poises. In the writer's laboratory the values for fourteen steam- and vacuum-refined asphalts have been found to vary from 14,000 to 30,000 poises. Saal (94) found that at the Ring and Ball softening points the asphalts which he investigated had viscosities from 10,000 to 20,000 poises. Although all of the tests commonly used to measure the consistency of bitumens are related in some way to the viscosity expressed in c.g.s. units, the relationship is usually very complex.

A number of instruments are available for measuring the consistency, in arbitrary units, of soft bitumens at atmospheric temperatures or of hard ones at elevated temperatures. The Saybolt-Furol and Saybolt-Universal efflux viscometers and the Stormer and MacMichael rotating machines are widely used in the United States. The Redwood is used in England, the Engler in Germany, and the Barbey viscometer to some extent in France. Each instrument has its own sphere of usefulness, and although none of them gives values in absolute units (poises) directly, conversion factors have been developed for some of the instruments which have proved to be quite satisfactory.

In recent years several methods have been devised or improved (110) for measuring the consistency of very viscous materials. Some of these instruments have been found useful in evaluating the flow properties of hard asphaltic bitumens at atmospheric temperatures. Saal (93) and Saal and Koens (92) have given excellent reviews of several of the available

methods, together with the consistency ranges over which each type of instrument is applicable.

The alternating-stress method developed by Bingham and Stephens (14), and used by them to measure the viscosity of rosin, has been employed (76, 106, 107) to obtain information concerning the consistencies of asphalts possessing viscosities above 10^5 poises. When consistencies below 10^5 are to be measured, a modification (76) of the Bingham-Murray tube plastometer is a convenient and accurate method. The rotating concentric cylinder type of viscometer (23), which has been modified recently (57), is adaptable to a very wide range of consistencies, and by means of this instrument the material under test may be subjected to a considerable range of shearing stress. A number of steam- and vacuum-refined oil asphalts of the consistency used in asphalt pavements have been found to behave essentially as viscous liquids. However, hard steam-refined and air-blown asphalts were found to give a curvilinear relation between rate of shear and shearing stress. Also, these materials are frequently elastic and thixotropic.

Saal and Koens (92) also studied the flow properties of several bitumens by means of capillary and rotating concentric cylinder viscometers, and found most of them to be non-Newtonian liquids, i.e., the experimentally determined viscosities decreased with increasing shearing stress. With some of the asphalts they found evidence for the existence of thixotropy; the bitumens showed a decrease in consistency with mechanical working. The phenomenon of thixotropy is probably caused by the elimination of structure within the asphalt. Results obtained in the research laboratories of The Barber Asphalt Company indicated that the amount of structure, which appeared in the form of thixotropy, varied among different asphalts and could be increased markedly by the addition of finely ground mineral powders to the bitumen.

Viscosity was related to the penetration by Saal (93) by means of the expression:

$$\text{Viscosity (poises)} = \frac{9.1 \times 10^9}{(\text{penetration})^{1.93}} \quad (2)$$

where the viscosity and penetration were determined at the same temperature. However, Traxler, Pittman, and Burns (106) found that such an expression did not accurately relate the penetration and viscosity of several kinds of asphaltic bitumen. No doubt the penetration of a needle into a mass of asphalt is greatly influenced by the adhesiveness of the bitumen toward the steel. This may be the chief reason why, for all kinds of bitumen, penetration cannot be expressed as a simple function of viscosity.

The change of viscosity of asphaltic bitumen with temperature is a

very important property. Walther proposed a formula of the type

$$\log \log (V_k + 1) = m \log T + c \quad (3)$$

where V_k = kinematic viscosity in centistokes, T = absolute temperature ($273 + ^\circ\text{C}.$), and m and c are constants. It is admitted that this formula may be criticized because of the double logarithm, and over a wide range of temperatures it has been found (76) to give values which deviate from those determined experimentally by as much as 25 to 30 per cent. Duplicate experiments checked within about 5 per cent.

Using a rotating viscometer, Umstatter (114) investigated the influence of temperature on the viscosity of asphalts over the temperature range of 25° to $50^\circ\text{C}.$, and obtained a straight line by plotting the logarithm of the

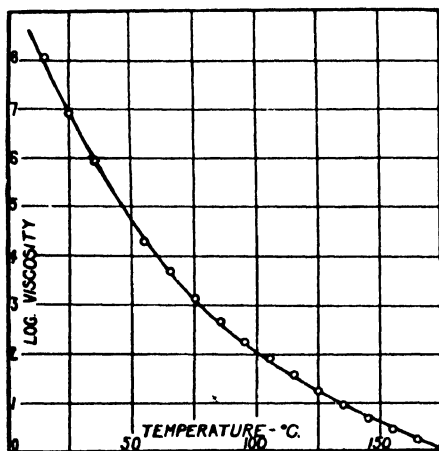


FIG. 1. Variation of viscosity with temperature for a Mexican asphalt

viscosity against the reciprocal of the square of the absolute temperature. However, when temperature viscosity data obtained over a wide range of temperature are tested in the manner proposed by Umstatter, it is found that the curve breaks in the region of the softening point of the asphalt.

Although some investigators have found transition points in the viscosity-temperature relationships for asphalts, there are ample data indicating a distinct continuity throughout a wide temperature range. Figure 1 shows the log viscosity versus temperature relationship (76) of an asphalt prepared from Mexican petroleum in a batch steam still. The penetration of the asphalt at $25^\circ\text{C}.$, 100 g., and 5 sec. was 62; the Ring and Ball softening point was $52.2^\circ\text{C}.$ The smooth curve obtained over the wide range of viscosities is a good indication of the accuracy of the methods of measure-

ment used. Further, the curve indicates that a gradual change occurs in the physical state of the asphalt as the temperature is raised or lowered.

Numerous empirical methods have been proposed for evaluating the susceptibility (change of consistency with temperature) of asphalts. Most of these methods have been reviewed and criticized (107), and the proposal made that the susceptibility of an asphalt be expressed as a function of the slope of some linear temperature viscosity relation. Although the most simple expression would be the slope of an arithmetical plot of temperature against viscosity, such a plot is not linear even over a short temperature range. However, for most asphalts a plot of the logarithm of viscosity against temperature is essentially a straight line for limited temperature ranges above and below the softening point. The asphalt viscosity index proposed was expressed as

$$A. V. I. = 100 \left(\frac{\eta_c}{\eta_d} \right)^{\frac{1}{t_c - t_d}} - \quad (4)$$

where η_c and η_d are the viscosities, in poises, of the asphalt at temperatures ($^{\circ}\text{C}.$) t_c and t_d , respectively.

The *A. V. I.* evaluates the percentage change in the viscosity of an asphalt for a $1^{\circ}\text{C}.$ rise in temperature. To obtain the index for a particular asphalt it is only necessary to determine experimentally the viscosities at two temperatures within a range where a plot of log viscosity against temperature gives a straight line. Indices may be developed for a given asphalt for temperature ranges both above and below the softening point. The former is of interest in the processing of asphaltic materials, whereas the latter is helpful in evaluating their behavior under service conditions.

Recently Nevitt and Krehma (68) developed an expression based on an equation similar to equation 3, by which they evaluated the susceptibility of a number of asphalts over a wide temperature range. Also, a new application of the penetration test to the measurement of the susceptibility of asphalts to temperature has been given by Bencowitz and Boe (12). They found that the equation

$$p = A + B \times C^t \quad (5)$$

where p = penetration in decimillimeters, t = temperature in degrees Centigrade, and A , B , and C are constants characteristic of each asphalt, held for asphalts of different sources and methods of processing.

The viscosities of bitumens were measured, years ago, by Pochettino (77), who employed a capillary viscometer and the falling coaxial cylinder viscometer proposed by Segel (98). The falling-cylinder viscometer has been used to evaluate asphalts possessing consistencies above 10^5 poises;

thus it may be used over about the same range as the alternating stress method discussed above. Further, the method has been adapted (111) to a study of the increase of consistency with time, which is a characteristic of most bitumens. After a bitumen has been melted and allowed to cool, a progressive hardening occurs, which varies markedly with the type and the source of the material used. However, the rate of hardening decreases rapidly with time. This increase in viscosity is not due to loss of volatile constituents, because careful reheating and cooling will return the bitumen to its original consistency. Mechanical working of the asphalt will have the same effect as heating, but to a lesser degree, indicating that time-hardening is a manifestation of thixotropy.

TABLE 4
Increase of viscosities of asphalts with time

ASPHALT	ELAPSED TIME AFTER COOLING	VISCOSITY AT 25°C.
	hours	poises $\times 10^{-4}$
A	3	2 11
	24	2 12
	51	2 14
	96	2 14
	168	2 18
	336	2 25
	936	2 26
	2523	2 32
F	3 5	3 98
	24	4 29
	48	4 48
	75	4 62
	148	4 80
	240	5 04
	507	5 30

In the experimental study of the "time-hardening" of asphaltic bitumens a number of falling coaxial cylinder viscometers were filled simultaneously with a particular bitumen. The loaded viscometers were placed in an air bath maintained at $25^{\circ} \pm 1^{\circ}\text{C}$. Individual instruments were removed from time to time, and viscosity determinations made at 25°C . Table 4 gives the data on two asphaltic bitumens having greatly different time-hardening characteristics. Asphalt A, produced by the vacuum distillation of a Californian petroleum, had a penetration of 55 at 25°C ., 100 g., 5 sec., and a Ring and Ball softening point of 47.2°C . Asphalt F, produced by batch steam distillation of a mixture of heavy gravity with some medium gravity petroleum from the Mene Grande field in Venezuela, had a pene-

tration of 63 at 25°C., 100 g., 5 sec., and a Ring and Ball softening point of 51.7°C.

Data similar to those given in table 4 have been obtained for a number of different asphalts, and it appears that both the source and method of processing have a profound influence on the degree of hardening exhibited by the various bitumens. Since the bitumens which show the most hardening with time are the ones which also give the greatest deviations from viscous flow, it may be concluded that the degree of extent of this hardening is dependent upon the amount of "structure" potentially present in the material.

Although the elasticity of asphaltic bitumen and bituminous plastics is undoubtedly an important property, comparatively little work has been done toward its evaluation. In all measurements of the flow of bitumens of high consistency at ordinary atmospheric temperatures elastic effects are apparent. The harder the asphalt or the lower the temperature, the more evident these effects become (109), because the permanent (viscous or plastic) deformation being small obscures to a lesser extent the non-permanent (elastic) deformation of the sample.

Pochettino (77) investigated the elasticity of asphaltic bitumens and tars by means of an acoustical method. Recently Rader (79) measured the moduli of elasticity in beams of asphaltic paving mixtures at very low temperatures. The method used was similar to that employed in determining flexure in beams of the usual structural materials. Some preliminary work has been done in estimating the elasticity of compression in asphalt paving mixtures (108, 116). Efforts have been made to increase the elasticity of asphaltic bitumens by the addition of rubber and other materials. German patent 578,934 proposes to improve the elasticity of asphaltic masses by the addition of China wood oil and a condensing agent such as aluminum chloride or ferric chloride. Gemant (34) found that mineral oils possess elasticity, and he ascribes the effect to a fine lattice work of colloidal particles within which the liquid phase is held.

From the above outline it must be admitted that although rapid advancements have been made during recent years, our understanding of the physical chemistry of asphaltic bitumen is still quite elementary. The chaotic condition of the information concerning the various phases of the problem is mainly due to (1) the complex composition of asphalt, (2) the fact that asphalt from various sources and processed by different methods varies greatly, and (3) the fact that the determination of any property is frequently influenced directly or indirectly by one or more characteristics.

X. REFERENCES

- (1) ABRAHAM: *Asphalts and Related Substances*, 2nd edition. D. van Nostrand Company, New York (1929).
- (2) ABSON: *Proc. Am. Soc. Testing Materials* **33**, II, 704 (1933).

- (3) ALEXANDER: J. Ind. Eng. Chem. **2**, 242 (1910).
- (4) Am. Soc. Testing Materials, Method D5-25.
- (5) Am. Soc. Testing Materials, Method D36-26.
- (6) Am. Soc. Testing Materials, Method D139-27.
- (7) BAIN: Chem. Ind. **47**, 552 (1928).
- (8) BARTELL AND MILLER: Ind. Eng. Chem. **20**, 738 (1928).
- (9) BARTELL AND MILLER: Ind. Eng. Chem. **24**, 335 (1932).
- (10) BATEMAN AND DELP: Proc. Am. Soc. Testing Materials **27**, 11, 465 (1927).
- (11) BATEMAN AND LEHMAN: Proc. Am. Soc. Testing Materials **29**, 11, 943 (1929).
- (12) BENCOWITZ AND BOE: Ind. Eng. Chem., Anal. Ed. **8**, 157 (1936).
- (13) BENTZ AND STROBEL: Proc. World Petroleum Congress (London) I, 334 (1933).
- (14) BINGHAM AND STEPHENS: Physics **5**, 217 (1934).
- (15) BIRD AND CALCOTT: Bull. Phil. Soc., University of Virginia. Science series I, 365 (1914).
- (16) BOSSHARD AND WILDI: Helv. Chim. Acta **13**, 572 (1930).
- (17) BRANNT: Petroleum, its History, Origin, Occurrence, Production, Physical and Chemical Constitution, Technology, Examination and Uses. Henry Carey Baird and Co., Philadelphia (1895).
- (18) BRAY AND BAHLKE: Propane Processes for Refining of Lubricating Oil: I. Deasphalting. Presented before the Petroleum Division of the American Chemical Society, at the meeting held in San Francisco, August 19-23, 1935.
- (19) BROOKS: J. Inst. Petroleum Tech. **20**, 177 (1934).
- (20) BRUCKNER AND MEISHARD: Petroleum Z. **29**, 8 (1933).
- (21) CHERNOZHUKOV: Neftyanoye Khozaystvo **15**, 670 (1928).
- (22) CHRISTOPHER: Western Gas **8**, 16 (1932).
- (23) COUETTE: Ann. chim. phys. [6] **21**, 433 (1890).
- (24) DAHLBERG: Asphalt Teer Strassenbautech. **34**, 585 (1934).
- (25) DEMAREST AND RIEMAN: Ind. Eng. Chem., Anal. Ed. **3**, 15 (1931).
- (26) DOW: Pit and Quarry **16**, 88 (1928).
- (27) ENGLER AND STEINKOPF: Ber. **47**, 335 (1914).
- (28) ERRERA: Trans. Faraday Soc. **19**, 314 (1923).
- (29) FERRIS AND McILVAIN: Ind. Eng. Chem., Anal. Ed. **6**, 23 (1934).
- (30) First Report on Viscosity and Plasticity, prepared by the Committee for the Study of Viscosity of the Academy of Science at Amsterdam, page 148. Uitgave van de N.V. Noord-Hollandsche Uitgevers Maatschappij, Amsterdam (1935).
- (31) FRANCIS AND BENNETT: Ind. Eng. Chem. **14**, 626 (1922).
- (32) FRICKE AND MEYRING: Asphalt Teer Strassenbautech. **32**, 264 (1932).
- (33) FRIEDMAN: Erdöl u. Teer **6**, 285, 301 (1930).
- (34) GEMANT: Sitzber. preuss Akad. Wiss., April 28, 1932, p. 168.
- (35) GILPIN AND SCHNEEBERGER: Am. Chem. J. **50**, 59 (1913).
- (36) GÖDRICH: Monatsh. **36**, 535 (1915).
- (37) GRAEFE: Petroleum Z. **31**, 1 (1935).
- (38) GUISELIN AND HANDRICOURT: Petroleum Rev. **27**, 151 (1912).
- (39) HACKFORD: J. Inst. Petroleum Tech. **18**, 74 (1932).
- (40) HENDERSON: Science **81**, 176 (1935).
- (41) HIBBEN: Ind. Eng. Chem. **26**, 646 (1934).
- (42) HRADIL: Petroleum Z. **30**, 1 (1934).
- (43) JAEGER: Z. anorg. allgem. Chem. **101**, 46 (1917).
- (44) JOHANSEN: Ind. Eng. Chem. **16**, 132 (1924).
- (45) KATZ: Can. J. Research **10**, 435 (1934).

- (46) KEITH AND FORREST: *Trans. Am. Inst. Chem. Engrs.* **30**, 329 (1934).
- (47) KINDSCHER: *Bitumen* **3**, 104 (1933).
- (48) LEE: *J. Soc. Chem. Ind.* **55**, 23T (1936).
- (49) LINDGREN: *Econ. Geol.* **18**, 419 (1923).
- (50) MABERRY: *Proc. Am. Phil. Soc.* **42**, 36 (1900).
- (51) MACFARLANE: *Fishes, the Source of Petroleum*. The MacMillan Company, New York (1923).
- (52) MACHT: *Erdöl u. Teer* **7**, 225 (1931).
- (53) MACK: *J. Phys. Chem.* **36**, 2901 (1932).
- (54) MACKENZIE: *J. Ind. Eng. Chem.* **2**, 124 (1910).
- (55) McLEAN AND KOHMAN: *Elec. Eng.* **53**, 255 (1934).
- (56) MARCUSSON: *Chem. Ztg.* **39**, 1243 (1915).
- (57) MOONEY AND EWART: *Physics* **5**, 356 (1934).
- (58) NELLENSTEYN: *Chem. Weekblad* **21**, 42 (1924).
- (59) NELLENSTEYN: *J. Inst. Petroleum Tech.* **10**, 311 (1924).
- (60) NELLENSTEYN AND VAN DER BURGH: *J. Inst. Petroleum Tech.* **11**, 346 (1925).
- (61) NELLENSTEYN: *J. Inst. Petroleum Tech.* **14**, 134 (1928).
- (62) NELLENSTEYN AND ROODENBURG: *Kolloidchem. Beihefte* **31**, 434 (1930).
- (63) NELLENSTEYN: *Chem. Weekblad* **28**, 313 (1931).
- (64) NELLENSTEYN AND THOENS: *Chem. Weekblad* **30**, 359 (1933).
- (65) NELLENSTEYN AND ROODENBURG: *Kolloid-Z.* **63**, 339 (1933).
- (66) NELLENSTEYN: *Proc. World Petroleum Congress II*, 616 (1933).
- (67) NELLENSTEYN: *7th Permanent International Association of Road Congresses*, No. 31, Munich (1934).
- (68) NEVITT AND KACHMA: *Petroleum Division, Ninety-first Meeting of the American Chemical Society, Kansas City, April, 1936*.
- (69) NÜSSEL AND NEUMAN: *Bitumen* **5**, 125 (1935).
- (70) OBERLE: *Allgem. Österr. Chem. Tech. Ztg.* **48**, 129 (1930).
- (71) OLIENSIS: *Proc. Am. Soc. Testing Materials* **33**, II, 715 (1933).
- (72) ORLOV AND USPENSKI: *J. Applied Chem. U. S. S. R.* **6**, 1010 (1933).
- (73) PAILLAR: *J. Ind. Eng. Chem.* **6**, 286 (1914).
- (74) PEEK AND McLEAN: *Ind. Eng. Chem., Anal. Ed.* **6**, 85 (1934).
- (75) PECKHAM: *Solid Bitumens, their Physical and Chemical Properties and Chemical Analysis together with a Treatise on the Chemical Technology of Bituminous Pavements*. The Myron C. Clark Publishing Co., New York (1909).
- (76) PITTMAN AND TRAXLER: *Physics* **5**, 221 (1931).
- (77) POCETTINO: *Nuovo cemento* **8**, 77 (1914).
- (78) PÖLL: *Petroleum Z.* **27**, 817 (1931).
- (79) RADER: *Proc. Am. Soc. Testing Materials* **35**, II, 559 (1935).
- (80) RAE: *Trans. Am. Inst. Min. Met. Engrs.* **68**, 1112 (1923).
- (81) RAKUZIN: *Zhur. Russk. Fiz. Khim. Obsch.* **35**, 554 (1904).
- (82) REDWOOD: *A Treatise on Petroleum*, Vol. I, 4th edition. Charles Griffin and Co. Ltd., London (1922).
- (83) REEVE AND LEWIS: *J. Ind. Eng. Chem.* **9**, 743 (1917).
- (84) RICHARDSON AND FORREST: *J. Soc. Chem. Ind.* **24**, 7 (1905).
- (85) RICHARDSON: *The Modern Asphalt Pavement*, 2nd edition. John Wiley and Sons, New York (1908).
- (86) RICHARDSON: *J. Ind. Eng. Chem.* **8**, 4 (1916).
- (87) RICHARDSON: *Chem. Met. Eng.* **16**, 3 (1917).

- (88) RIEDEL AND WEBER: Asphalt Teer Strassenbautech. **33**, 677 (1933).
- (89) RIEHM: Proc. World Petroleum Congress II, 552, London (1933).
- (90) ROSINGER: Kolloid-Z. **15**, 177 (1914).
- (91) SAAL: Bitumen **3**, 101 (1933).
- (92) SAAL AND KOENS: J. Inst. Petroleum Tech. **19**, 176 (1933).
- (93) SAAL: Proc. World Petroleum Congress II, 515, London (1933).
- (94) SAAL: Chem. Weekblad **32**, 435 (1935).
- (95) SAAL: Chem. Weekblad **32**, 486 (1935).
- (96) SCHWARZ: Asphalt und Strassenbau No. 5. Supplement of Petroleum Z. **28** (1932).
- (97) SCHWARZ: Allgem. Österr. Chem. Tech. Ztg. **51**, 41 (1933).
- (98) SEGEL: Physik. Z. **4**, 493 (1903).
- (99) SIKES AND COREY: Ind. Eng. Chem. **27**, 192 (1935).
- (100) STEINKOPF AND WINTERNITZ: Chem. Ztg. **38**, 613 (1914).
- (101) STRIETER: Dissertation, Columbia University, 1925.
- (102) TAUSZ: Petroleum Z. **14**, 553 (1919).
- (103) TRAXLER: J. Phys. Chem. **32**, 127 (1926).
- (104) TRAXLER AND PITTMAN: Ind. Eng. Chem. **24**, 1003, 1391 (1932).
- (105) TRAXLER AND HUNTZICKER: J. Phys. Chem. **39**, 431 (1935).
- (106) TRAXLER, PITTMAN, AND BURNS: Physics **6**, 58 (1935).
- (107) TRAXLER AND SCHWEYER: Physics **7**, 67 (1936).
- (108) TRAXLER: Ind. Eng. Chem., Anal. Ed. **8**, 185 (1936).
- (109) TRAXLER AND COOMBS: Thirteenth Colloid Symposium, held at St. Louis, June 11-13, 1936.
- (110) TRAXLER AND SCHWEYER: Preprint No. 86 for the Annual Meeting of American Society for Testing Materials, June 29-July 3, 1936.
- (111) TRAXLER AND SCHWEYER: Preprint No. 88 for the Annual Meeting of the American Society for Testing Materials, June 29-July 3, 1936.
- (112) TREIBS: Ann. **510**, 42 (1934).
- (113) TYCININ: Neftyanoe Khozyaistvo **4**, 73 (1923).
- (114) ÜMSTATTER: Kolloid Beihefte **39**, 265 (1934).
- (115) VELLINGER: Petroleum **31**, 17 (1935).
- (116) VOKAC: Preprint No. 89 for the Annual Meeting of the American Society for Testing Materials, June 29-July 3, 1936.
- (117) WATERMAN AND NELLENSTEYN: J. Inst. Petroleum Tech. **11**, 81 (1925).
- (118) WEDMORE: Proc. World Petroleum Congress II, 593, London (1933).
- (119) WEISS AND VELLINGER: Compt. rend. **188**, 901, 1099 (1929).
- (120) WILHELMI: Proc. World Petroleum Congress II, 619, London (1933).
- (121) ZALARIU AND LUCATU: Bull. soc. chim. Romania **12**, 90 (1930).
- (122) ZALOGIECHI AND ZIELENFELT: 8th International Congress of Applied Chem. **10**, 335 (1912).
- (123) ZELINSKII AND KOSLOV: Ber. **64B**, 2130 (1931).
- (124) ZWERGAL: Oel und Kohle **11**, 608 (1935).

THE THERMAL STABILITY OF PARAFFINIC AND OLEFINIC HYDROCARBONS

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The relative stability of hydrocarbons determines the course of the pyrolytic reactions, a complete knowledge of which would make possible the choice of optimum conditions for obtaining desired hydrocarbons and would simplify the formulation of the mechanism of the reaction. Unfortunately, strictly comparable data are not wholly available. However, by a comparison of the results obtained on paraffins and olefins under comparable conditions, their relative stabilities can be estimated with some order of accuracy. Furthermore, when the results are not obtained under comparable conditions, a comparison of conclusions gives the next best order of stability.

A small per cent conversion of hydrocarbons would offer a basis for a comparison of their stabilities, since under this condition secondary reactions would not be present or would be negligible. Some investigators have utilized this method, while others have produced maximum yields of liquids or gases, obtaining decomposition up to 100 per cent. These latter results often give conclusions which contradict the ones obtained at low per cent conversion.

STABILITY OF PARAFFINIC HYDROCARBONS

Different stabilities for the lower paraffins were recognized by the earliest investigators, yet it remained for experimenters in the last decade or so, using the better analytical methods available, to obtain the decomposition data from which results might be reasonably compared.

The stability of paraffins depends upon their ability to withstand decomposition and isomerization. Only the resistance to decomposition has been reported, and therefore can be used as a basis for comparison. From this viewpoint, the stability of the normal and isoparaffins through hexane decreases with an increase in molecular weight. However, the stability of the iso versus the normal paraffin is not so well defined, because isobutane is more stable than *n*-butane, except that they are the same at 600°C., while isopentane is less stable than *n*-pentane and 2-methylpentane is less stable than *n*-hexane.

The data for pyrolysis of normal paraffins are summarized in table 1 and show that for a given set of conditions the shorter the chain the greater the resistance to heat. Hence, it is concluded that through *n*-hexane the stability decreases with increasing chain length.

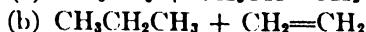
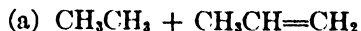
The initial decomposition temperatures of some paraffins were obtained by noting the pressure change (17, 19, 20) when the hydrocarbons were heated for one hour in a glass bulb. It was claimed that specific products were formed for a restricted range of temperatures. Thus, for *n*-butane

TABLE 1
Pyrolysis of normal paraffinic hydrocarbons

CONDITIONS			HYDROCARBON, PER CENT DECOMPOSITION						REFERENCE NO.
Temp.	Time	Pressure	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	
°C.		atm.							
430	8.9-9.0 hrs.	1 0				6 0			5
430	4.0 hrs.	1 0					5.0		
430	2.0 hrs.	1 0						8 0	
650	12 sec.	1.0		6 0					21
650	11 sec.	1.0			16 0				
650	10 sec.	1 0				32 7			
950	Constant	1 0		35 8	48 7	63 0			1
HYDROCARBON, PER CENT EXPANSION									
725	Constant	1.0						Complete decomposition	6
750	Constant	1 0		63.0	88.8	103 6	Complete decomposition		6
950	Constant	1 0	3 7	87 5	144 0	215 0			6
1100	3.2×10^{-3} sec.	(50 mm.)			109.0				
1100	2.5×10^{-3} sec.	(50 mm.)		86 0		158 0			26
1400	3.0×10^{-3} sec.	(50 mm.)	28.0	186 0	246 0				26

the initial temperature of decomposition was found to be 400°C. In the first temperature range, from 400° to 450°C., the products were methane and propene; from 450° to 499°C. ethane and ethylene were additional products, the breaking of the 2-3 carbon-to-carbon bond being characteristic of this temperature range; above 499°C., hydrogen and butene were obtained in addition to the above hydrocarbons. These results were not confirmed (11) in a flow method at 365°C., owing to formation of ethane, ethylene, and hydrogen along with the predicted methane and propene. The results obtained with *n*-pentane (17, 19, 20) by the bulb method indi-

cated that the initial decomposition temperature was 391°C.; between 391° and 426°C. two groups of hydrocarbons were found in the ratio of 4 of group a to 1 of group b:



The second range of temperature was 426° to 450°C., the products of which included those obtained in the first range plus methane and unidentified butenes. The third range was 450° to 499°C., and the products consisted of the above hydrocarbons plus hydrogen and possibly a pentene. Evidence against these claims was obtained (5) when *n*-pentane was pyrolyzed at 396°C., yielding C_1 , C_2 , C_3 , C_4 , and C_5 hydrocarbons and hydrogen.

TABLE 2
Pyrolysis of straight- and branched-chain paraffins

CONDITIONS			HYDROCARBON, PER CENT DECOMPOSITION					REFERENCE
Temp.	Time	Pressure	<i>n</i> - C_4H_{10}	iso- C_4H_{10}	<i>n</i> - C_5H_{12}	iso- C_5H_{12}	neo- C_5H_{12}	
°C	seconds	atmospheres						
555	82.3	48.29	56.0					28
555	86.5	48.39		26.0				
560	16.6	0.1				8.25		5
575	20.5	0.087					4.0	5
575	16.1	0.1			4.9			5
600	30.0	1.0	22.0					12
600	27.0	1.0		22.0				12
650	10.0	1.0	32.7					21
650	11.0	1.0		26.7				21
			HYDROCARBON, PER CENT EXPANSION					
1100	2.5×10^{-3}	(50 mm.)	158.0	142.0				

In spite of the disagreement concerning the relative stabilities of different carbon-to-carbon bonds in normal butane and normal pentane, the data offer a comparison of the initial decomposition temperatures of those hydrocarbons studied, since the experiments were made under comparable conditions. Thus, the results show that the stabilities of butane (400°C.), pentane (391°C.), and hexane (343°C.) decrease in this order.

Data on the relative stability of straight- and branched-chain paraffins are presented in table 2, which shows that *n*- and iso-butane have the same stability at 600°C., a result which should be checked, because at 555°, 650°, and 1100°C. isobutane is the more stable. Furthermore, it is shown that when isobutane is the more stable, it is so by a small margin except at

555°C. and 48.39 atmospheres pressure. Hence, it is concluded that at low pressure isobutane is slightly more stable, while under high pressure it is more than twice as stable as *n*-butane. In table 2 there are also data

TABLE 2a
Decomposition of paraffins
(20 per cent)

HYDROCARBON	TEMPERATURE	TIME	PRESSURE
	°C	seconds	atmospheres
C ₃ H ₈ ...	600	35	1
C ₃ H ₈	600	28	7
C ₄ H ₁₀ ...	650	10 0	1
C ₄ H ₁₀ ...	650	5 9	7
C ₅ H ₁₂ ...	700	1 3	1
C ₅ H ₁₂	700	2 0	7
<i>n</i> -C ₄ H ₁₀ ...	600	17	1
<i>n</i> -C ₄ H ₁₀	600	13	7
<i>n</i> -C ₄ H ₁₀ ...	650	3 5	1
<i>n</i> -C ₄ H ₁₀ ...	650	3 2	7
iso-C ₄ H ₁₀ ...	650	4 0	1
iso-C ₄ H ₁₀	650	4 5	7

TABLE 3
Temperatures of initial decomposition of straight- and branched-chain paraffins

HYDROCARBON	TEMPERATURE
	°C.
Isobutane...	428
<i>n</i> -Butane...	400
<i>n</i> -Pentane...	391
Isopentane...	383
<i>n</i> -Hexane...	343
2-Methylpentane...	339

which show that the stability of neo-, *n*-, and iso-pentane decreases in the order named.

The effect of pressure upon the relative stability of propane, *n*-butane, and isobutane (3a) is shown in table 2a. At 600° and 650°C., pressure

reduces the resistance of propane and *n*-butane to decomposition, while at 650° and 700°C. in the case of the butanes the pressure effect is not so great.

A comparison of the initial decomposition temperatures of straight- and branched-chain paraffins (17) shows that isobutane is more stable than *n*-butane, while *n*-pentane is more stable than isopentane and *n*-hexane more than 2-methylpentane. It is concluded that as the molecular weight increases the difference in initial temperatures of decomposition for the normal and iso compounds decreases. The data which are recorded in table 3 show also that isobutane is more stable than isopentane, which is more stable than 2-methylpentane. It is, therefore, further concluded for the hydrocarbons discussed that the stability decreases with an increase in the molecular weight.

The stability of the first three members of the paraffin series is established, while the evidence for the C_4 , C_5 , and C_6 compounds is not so clear cut. However, the paraffins studied are placed in order of decreasing stability as follows: methane, ethane, propane, isobutane, butane, neopentane, *n*-pentane, isopentane, *n*-hexane, and 2-methylpentane.

Concerning the paraffins above the hexanes, the experiments (3) on the thermal decomposition of mixtures of hydrocarbons obtained by fractionating Pennsylvania petroleum which was made up largely of paraffins is to be noted. It was shown that stability was not always a direct function of the size of the paraffin molecule. It was concluded that "if stability is graphed against the boiling point of the paraffins, there results a curve having the maximum stability at about 250° representing the compounds $C_{12}H_{26}$ to $C_{15}H_{32}$, minima at the lowest boiling points (C_5H_{12} to C_9H_{20}), and the highest boiling points ($C_{19}H_{40}$ to $C_{23}H_{48}$)."

STABILITY OF OLEFINIC HYDROCARBONS

The olefinic hydrocarbons undergo three type reactions: (1) formation of higher hydrocarbons by polymerization or other reactions, (2) decomposition, and (3) isomerization.

Polymerization and formation of higher hydrocarbons

Polymerization is a characteristic reaction of the olefins. The primary effect of heat upon an olefin is activation of the double bond, since the average value of $39,000 \pm 4,000$ calories in the polymerization process is much lower than the activation energies of the other bonds for cracking reactions: $C=C$, 125,000; $C-C$, 79,500; $C-H$, 93,000 calories. The data of table 4 show the different values of the energies of activation of the $C=C$ bond in the polymerization process, and $39,000 \pm 4,000$ calories is taken as an average value. Thus, considering the energy of activation and assuming that the other energy requirements are satisfied, polymerization precedes decomposition, since the latter is so small that it can be neglected (27).

TABLE 4
Energies of activation

HYDROCARBON	ACTIVATED BOND	ENERGY OF ACTIVATION	REFERENCE NO.
		<i>calories</i>	
Ethylene	C=C	39,000 \pm 4,000	22
Ethylene	C=C	37,700 \pm 200	13
Propene	C=C	38,000 \pm 500	13
2-Butene	C=C	38,000 \pm 1,000	13
Isobutene	C=C	43,000 \pm 1,000	13
"Amylene"	C=C	38,000 \pm 2,000	13
Ethane	C-C	79,500	23
Methane	C-H	93,000	23

TABLE 5
Oil yield from olefinic hydrocarbons at constant feed rate

OLEFIN	TEMPERATURE	PERCENT CHANGE IN VOLUME	CRUDE OIL YIELD IN WEIGHT PER CENT OF GAS PASSED	PER CENT OF CHARGE DISAPPEARING
	$^{\circ}\text{C}$	<i>per cent</i>	<i>weight per cent</i>	<i>per cent</i>
Ethylene				
Propene				
1-Butene	600	-23.4	12.86	46.0
2-Butene	600	-25.40	5.20	35.0
Ethylene	650	-2.7	1.5	10.1
Propene	650	+4.0	5.25	13.1
1-Butene	650	-10.7	29.82	80.2
2-Butene	650	-7.46	27.00	80.0
Ethylene	700	-15.25	12.25	33.8
Propene	700	10.0	20.36	54.4
1-Butene	700	30.0	35.83	97.9
2-Butene	700	27.40	37.00	97.4
Ethylene	750	-16.40	28.24	52.4
Propene	750	20.0	35.60	89.6
1-Butene	750	43.90	39.62	98.7
2-Butene	750	38.90	39.62	97.9
Ethylene	800	-11.80	36.10	71.0
Propene	800	30.0	40.6	98.5
1-Butene	800	57.0	39.45	99.0
2-Butene	800	52.8	37.90	99.5

A similar conclusion, namely, that the formation of higher hydrocarbons is the predominant reaction, is reached from the data (2) of table 5, in which it is recorded that the volume decreases at 600° and 650°C. during the pyrolysis of 1- and 2-butene. Furthermore, the data at 600°, 650°, and 800°C. show that 2-butene is more resistant to oil formation than 1-butene, while at 700°C. the opposite is true, and at 750°C. they behave in the same way. The data show also that combination is the primary reaction for ethylene from 650° to 800°C. and that it undergoes this reaction to a smaller extent than propene, which in turn yields less oil than the butenes except at 800°C. Thus at 350°C. the order of decreasing stability toward the formation of higher hydrocarbons is: ethylene, propene, 2-butene, and 1-butene; at 800°C. propene and the butenes show about the same stability.

TABLE 6
Formation of higher hydrocarbons from olefinic hydrocarbons

HYDROCARBON	TEMPERATURE °C.	TIME OF CONTACT minutes	PRESSURE lbs. per sq. in.	CONVERSION weight per cent
Ethylene	371	18 7	2000	21 6
Propene	371	18 2	2000	5 6
Ethylene	395	6 5	3000	46 4
Propene	399	6 4	3000	12 7
Ethylene	455	5 3	3000	59 3
Propene	457	5 3	3000	43 4
Ethylene	456	4 1	500	20 6
Propene	455	5 7	500	16 3

It should be pointed out that the maximum yields of liquids from ethylene, propene, 1-butene, and 2-butene require temperatures of 810°, 790°, 775°, and 755°C., respectively. This shows that 1-butene is more stable than 2-butene by 20°C., which contradicts the above conclusion. This difference is probably due to difference in experimental methods used.

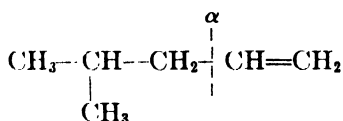
A comparison of the stabilities of ethylene and propene at pressures from 500 to 3000 lbs. per square inch showed (25) that ethylene was converted to liquids to a greater extent than propene when treated under the same conditions. This conclusion is opposite to the ones above, and it is difficult to explain except by differences in experimental method or pressure. The data are summarized in table 6.

Decomposition

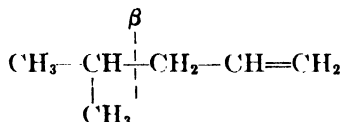
The second type reaction in pyrolyzing olefins is decomposition; in this connection the double-bond rule (24) should be mentioned. To illustrate

this rule, the pyrolysis of 1- and 2-butene (9) may be explained. Since the C=C bond is the point of strength during olefinic decomposition, the adjacent C—C bond (α) will be stronger relatively than the C—C bond one removed (β) from the C=C linkage, and alternate strong and weak C—C bonds will continue along the chain, the effect diminishing as the distance from the double bond is increased. Thus, for example, 1-butene, $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ is less stable than 2-butene, $\text{CH}_3\text{CH}=\text{CHCH}_3$, because the latter has no beta carbon-to-carbon bond.

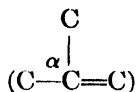
On the basis of this assumption the products obtained during the pyrolysis of 4-methyl-1-pentene (preponderance of propene over ethylene) are explained: if the α -bond is broken ethylene would be the most important product,



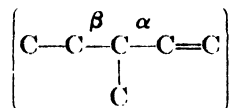
while if the β -bond broke then propene would be predominant.



The latter is the experimental fact and is in harmony with the rule. Furthermore, the greater stability of 2-butene ($\text{C}-\overset{\alpha}{\text{C}}=\overset{\alpha}{\text{C}}-\text{C}$) and isobutene



over 3-methyl-1-pentene (7)



is visualized when their skeletons are compared, since the latter has a $\overset{\beta}{\text{C}}-\text{C}$ bond. On the other hand, 1-butene is more stable than isobutene (27) at 1100°C. and the opposite is true at 650°C. (10).

The results obtained in decomposing olefins are recorded and discussed according to the experimental method used. Any differences in conclusions may be partly explained on this basis.

The initial temperatures and the relative extent of decomposition as

measured by means of a static (bulb) method show that ethylene is the most stable of the normal olefins studied, requiring the highest temperature of 380° to 400°C. The results (2) are summarized in tables 7 and 8, respectively, which show that the stability decreases in the order: ethylene, propene, 2-butene, and 1-butene.

Using a different experimental bulb method (20) the initial temperatures and extents of decomposition were measured for the pentenes (18). The

TABLE 7
Temperatures of initial decomposition of olefinic hydrocarbons
(Bulb method)

OLEFIN	TEMPERATURE RANGE	
	Lower	Upper
	*C.	*C.
Ethylene	380	400
Propene	357	375
2 Butene	350	375
1-Butene	325	350

TABLE 8
Per cent decomposition of olefinic hydrocarbons
(Bulb method)

TEMPERATURE	TIME	PER CENT DECOMPOSITION			
		C ₂ H ₄	C ₃ H ₆	1-C ₄ H ₈	2-C ₄ H ₈
*C	minutes				
375-580	360	0 0	2 0	7 4	5 3
500	45	6 8	11 5		
500	39			11 5	12 1
600	12	28 3	52 8		
600	9			58 7	53 2
700	1	25 8	64 8		

results showed that trimethylethylene was more stable than 2-pentene, which was more stable than 1-pentene.

The results (2) obtained in flow experiments are summarized in table 9, and show that from 650° to 900°C. the 1- and 2-butenes are of the same stability and that they are more susceptible to heat than propene and ethylene. At 600°C., however, 2-butene is more stable than 1-butene.

Other flow experiments (8, 9, 10), shown in table 10, include the work performed at 650° and 700°C. The results show that 2-pentene is less stable than isobutene at 700°C.; at 650°C. the order of decreasing stability is propene, isobutene, 2-butene, and 1-butene.

TABLE 9
Per cent decomposition of olefinic hydrocarbons
(Flow method: constant feed rate)

TEMPERATURE	PER CENT DECOMPOSITION			
	C ₃ H ₆	C ₄ H ₆	1-C ₅ H ₈	2-C ₅ H ₈
°C.				
600			45.9	35.0
650	10.1	13.0	80.2	80.0
700	33.8	54.4	97.9	97.4
750	52.4	89.6	98.7	97.9
800	71.0	98.5		
850	88.0		99.1	98.8
900	95.4		99.1	98.4

TABLE 10
Per cent decomposition of olefinic hydrocarbons
(Flow method)

TEMPERATURE	CONTACT TIME	PER CENT DECOMPOSITION				
		C ₃ H ₆	1-C ₄ H ₈	2-C ₄ H ₈	iso-C ₄ H ₈	2-C ₅ H ₁₀
°C.	seconds					
650	11.0		57.0			
650	13.0			44.0	11.1	
650	30.0	16				
700	4.1				21.0	
700	12.0				30.2	
700	3.5					83.0
700	11.4					91.0

The study (27) of the lower olefins at a high temperature (1100°C.) and short contact times (0.002 to 0.014 second) showed that they fall into two groups, namely, ethylene-propene and the butenes, the latter being less stable. The data show that ethylene is much more resistant to an increased contact time than propene and the butenes. The order of decreas-

ing stability is ethylene, propene, 2-butene, 1-butene, and isobutene. The lower stability of isobutene as compared with 1- and 2-butene is contradictory to the conclusion from table 10. Here, again, there may be some variable factor which thus far has eluded the various investigators and which is being recalled by "differences in the experimental method." However, it is to be noted, in this case, that there is a difference in the pressure. The results are summarized in table 11.

Isomerization

In connection with isomerization of the olefins, it has been shown that at 600° to 650°C. the isomerization of 1- and 2-butenes takes place with about the same ease (9). In the case of the pentenes, 1-pentene yields

TABLE 11

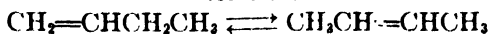
Per cent decomposition of olefinic hydrocarbons at 1100°C. and 50 mm. pressure

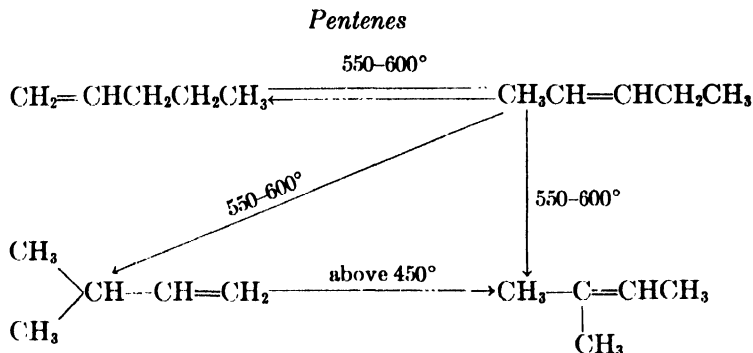
OLEFIN	CONTACT TIME × 10 ³	PER CENT DECOMPOSED	CONTACT TIME × 10 ³	PER CENT DECOMPOSED
	<i>seconds</i>	<i>per cent</i>	<i>seconds</i>	<i>per cent</i>
Ethylene	2.2	23.0	6.1	34.2
	4.1	24.0	14.0	46.2
Propene	2.2	27.4	5.8	65.6
	4.3	55.6	12.0	71.8
2-Butene	2.5	67.6	5.8	85.5
	3.0	77.2	11.0	91.0
1-Butene	1.9	69.6	7.9	89.9
	3.7	89.3	13.0	95.2
Isobutene	2.8	71.7	7.1	98.1
	4.0	92.2	11.0	100.0

2-pentene and vice versa (7) at 550° to 600°C., and under the same conditions isopropylethylene and trimethylethylene were formed from 2-pentene; above 450°C. isopropylethylene yielded trimethylethylene (18). Thus, it is observed that the branched pentenes are more resistant to heat than the normal pentenes, and that the normal butenes are more stable than the normal pentenes. These changes may be summarized as follows:

Butenes

600-650°C.





The study of the relative stability of the olefinic hydrocarbons is complicated by their ability to form higher hydrocarbons by polymerization or other reactions, decomposition, and isomerization.

The relative stability toward liquid formation has been measured from 600° to 800°C. At 600°C. the stability decreased as follows: ethylene, propene, 2-butene, and 1-butene; at 800°C. propene formed liquid to the same extent as 1- and 2-butene. Thus it is seen that with increasing temperatures these olefins approach the same stability. On the other hand, at 371° to 457°C. and high pressures ethylene is less stable toward polymerization than propene. These contradictory conclusions may be explained by differences in experimental method as well as by differences in the conditions.

The primary decomposition of olefins is negligible compared with the polymerization and is, therefore, not a fair measure of their relative stability. However, when based upon the extent of and initial temperatures of decomposition the following order of decreasing stability is estimated at 600° to 700°C.: ethylene, propene, isobutene, 2-butene, 1-butene, trimethylethylene, 2-pentene, and 1-pentene, while at 1100°C. isobutene was found to be less stable than 1-butene.

The meager data reported for the relative stability toward isomerization lead to the conclusion that 1- and 2-pentene are less stable than 1- and 2-butene. The pentene stability decreases in the order trimethylethylene, isopropylethylene, 2-pentene, and 1-pentene, while 1- and 2-butene are about equally stable.

The relative stability of the butenes offers a test of the double-bond rule. Thus isobutene and 2-butene should be more stable than 1-butene because the latter has a beta carbon-to-carbon bond. Such was found to be the case at 650°C., while at 1100°C. and 50 mm. pressure isobutene was the least stable.

STABILITY OF DIOLEFINIC HYDROCARBONS

The lower diolefins of both the allene and the conjugated types are generally more susceptible to polymerization and decomposition than monoolefins. Most of the study has been devoted to polymerization, but under conditions which permit of few comparisons.

Allene was found (16) to decompose to the extent of 80.5 per cent at 500°C. and 86 seconds contact time, 90 per cent of it forming liquid products. Methylallene, on the other hand, which was completely decomposed at 500°C. and a contact time of 36 to 37 seconds was converted (10) into 73.0 per cent liquid, the balance being gas. Thus, allene is more susceptible to polymerization and more resistant to decomposition than methylallene. Di-, tri-, and tetra-methylallenes polymerize (14,15) at about 150° to 175°C. if the contact time is long enough.

Butadiene slowly polymerizes at room temperature (29). The influence of the position of methyl groups on the polymerization of butadienes has been demonstrated (31) with the result that the dimethylbutadienes were found to possess stabilities increasing in the following order: 2,3-, 1,2-, 1,1-, 1,3-, and 1,4-dimethylbutadiene. Thus, as the methyl groups are moved from the center of the molecule the stability increases. The data are summarized in table 12. The tetra- and hexa-methylbutadienes possess less tendency to polymerize than do the dimethylbutadienes (31).

STABILITY OF PARAFFINIC AND OLEFINIC HYDROCARBONS

A comparison of the relative stability of the paraffins and olefins is only qualitative even when the best conditions are obtained, owing to the fact that the former undergo decomposition as the primary reaction, while the olefins polymerize and with them decomposition is a secondary reaction. Thus, in the following discussion the conclusions from different experimental results are occasionally contradictory, and a comparison would not be justified. It seems best, therefore, to interpret each set of data independently and to await improvement in experimental results before generalizing too sharply.

A comparison of the relative stability of the paraffins and olefins when based upon initial temperatures of decomposition as measured by a change of pressure when heated for six hours in a silica bulb shows that the paraffins are more stable. A summary of the results (2) is presented in table 13.

Using a static method and a heating time of one hour the C_6 olefins, except 1-pentene, were more stable than the corresponding paraffins. The data (17) are recorded in table 14.

The results of a direct comparison based upon per cent decomposition of isobutene and isobutane (12) are shown in table 15; from these results it was concluded that isobutene is the more stable.

The results summarized in table 16 show that at 1100°C. and a given contact time the expansion is greater from the pyrolysis of a paraffin (26)

TABLE 12
Polymerization of dimethylbutadienes
(At 100°C. for 30 days)

Position of methyl groups in dimethylbutadiene.....	2,3-	1,2-	1,1-	1,3-	1,4-
Per cent polymerized.....	100	91	57	51	33
Per cent converted to dimer.....	54	53	43	32	20
Per cent converted to higher polymer..	46	38	14	19	12
Mean molecular weight of higher polymers.....	1377	919	432	1334	795

TABLE 13
Temperatures of initial decomposition (°C.) of paraffinic and olefinic hydrocarbons

HYDROCARBON	TEMPERATURE RANGE	
	Lower	Upper
	°C.	°C.
Methane.....	540	675
Ethane.....	450	485
Propane.....	425	460
n-Butane.....	400	435
Ethylene.....	380	400
Propene.....	357	375
2-Butene.....	350	375
1-Butene.....	325	350

TABLE 14
Initial temperatures of decomposition of paraffinic and olefinic hydrocarbons

HYDROCARBON	INITIAL TEMPERATURE OF DECOMPOSITION
	°C.
1-Pentene.....	389
2-Pentene.....	400
n-Pentane.....	391
2-Methyl-2-butene.....	433
2-Methylbutane.....	383

than from the corresponding olefin (27). However, it should be pointed out that an olefin cannot be completely decomposed to yield as great an

expansion as a paraffin, because each mole of olefin contains 1 less mole of hydrogen than the corresponding paraffin.

The data (2) of table 17 lead to the same conclusion as those of table 16.

TABLE 15
Decomposition of isobutene and isobutane

HYDROCARBON	TEMPERATURE	CONTACT TIME	DECOMPOSITION
	°C.	seconds	per cent
Isobutane.....	600	24-26	20-25
Isobutene.....	600	18	1.2
Isobutene.....	600	198	20.0

TABLE 16
Per cent expansion at 1100°C. of paraffinic and olefinic hydrocarbons

HYDROCARBON	EXPANSION	CONTACT TIME × 10 ³
	per cent	seconds
Ethane.....	86	2.5
Propane.....	109	3.2
Isobutane.....	142	2.5
n-Butane.....	158	2.6
Ethylene.....	3	4.1
Propene.....	24	4.3
2-Butene.....	62	2.5
1-Butene.....	65	3.7
Isobutene.....	95	2.5

TABLE 17
Per cent expansion at constant feed rate of paraffinic and olefinic hydrocarbons

TEMPERATURE IN °C.	PER CENT EXPANSION FOR EACH HYDROCARBON						
	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	n-C ₆ H ₁₄	1-C ₄ H ₈	2-C ₄ H ₈
700	32.7	-15.25	52.5	10.0	87.5	30.0	27.4
750	63.0	-16.40	88.8	20.1	103.6	43.9	38.9
800	63.9	-11.80	105.0	30.1	140.0	57.0	52.8
850		+1.3	106.0	46.2		73.9	68.3
900	71.0	+13.1	119.0	64.2		104.0	100.0

From table 18 it is concluded that under atmospheric pressure the olefins yield maximum quantities of liquids at a temperature from 65° to 85°C. lower than the corresponding paraffins, but it is to be noted that the

paraffins must partly, at least, undergo decomposition before liquids can be formed.

Specific conclusions concerning the relative stability of paraffins and olefins can be made only from strictly comparable data which are not available as yet. Even a comparison of the conclusions based upon present information leads to some inconsistencies. In order, therefore, to obtain the valuable data that measurement of relative stability offers, further and more complete investigations are necessary.

TABLE 18

Temperature of maximum production (2) of liquid from paraffinic and olefinic hydrocarbons at atmospheric pressure

HYDROCARBON	TEMPERATURE FOR MAXIMUM LIQUID
	°C.
Ethane.....	890
Propane.....	865
<i>n</i> -Butane.....	840
Ethylene.....	810
Propene.....	790
1-Butene.....	775
2-Butene.....	755

CONCLUSIONS

1. The relative stability of the paraffins toward decomposition decreases in the following order: methane, ethane, propane, isobutane, butane, neopentane, *n*-pentane, isopentane, *n*-hexane, and 2-methylpentane.

2. At 600°C. the stability of the olefins toward the formation of higher hydrocarbons decreases in this order: ethylene, propene, 2-butene, and 1-butene; at higher temperatures the specific behavior is lost and they are of the same order of stability. At 371° to 457°C. under high pressure, ethylene is less stable than propene. These differences are probably due to different experimental methods or conditions.

3. Toward decomposition the following order of decreasing stability is estimated at 600° to 700°C.: ethylene, propene, isobutene, 2-butene, 1-butene, trimethylethylene, 2-pentene, and 1-pentene; isobutene was found to be less stable than 1-butene at 1100°C. and 50 mm. pressure.

4. Toward isomerization 1- and 2-pentene are less stable than 1- and 2-butene, which are about the same. The pentene stability decreases in the order: trimethylethylene, isopropylethylene, 2-pentene, and 1-pentene.

5. The diolefins are more susceptible to polymerization than the mono-

olefins. The dimethylbutadienes become more stable as the methyl groups are moved from the center of the molecule.

6. Specific conclusions as to the relative thermal stabilities of paraffins and olefins are not wholly warranted as yet, because strictly comparable data are unavailable.

REFERENCES

- (1) CAMBRON AND BAYLEY: *Can. J. Research* **9**, 175 (1933).
- (2) DUNSTAN, HAGUE, AND WHEELER: General Notes on the Pyrolysis of Paraffinic and Olefinic Hydrocarbons. (Private communication.)
- (3) EGLOFF AND MOORE: *Chem. Met. Eng.* **16**, 47 (1917).
- (3a) EGLOFF, THOMAS, AND LINN: Paper presented before the Organic Division at the Ninety-first Meeting of the American Chemical Society, held in Kansas City, April 13-17, 1936.
- (4) EGLOFF AND WILSON: *Ind. Eng. Chem.* **27**, 917 (1935).
- (5) FREY AND HEFF: *Ind. Eng. Chem.* **25**, 441 (1933).
- (6) HAGUE AND WHEELER: *J. Chem. Soc.* **1929**, 378; *Fuel* **8**, 560 (1929).
- (7) HURD: *Ind. Eng. Chem.* **26**, 50 (1934).
- (8) HURD AND EILERS: *Ind. Eng. Chem.* **26**, 776 (1934).
- (9) HURD AND GOLDSBY: *J. Am. Chem. Soc.* **56**, 1812 (1934).
- (10) HURD AND MEINERT: *J. Am. Chem. Soc.* **53**, 289 (1931).
- (11) HURD, PARRISH, AND PILGRIM: *J. Am. Chem. Soc.* **55**, 5016 (1933).
- (12) HURD AND SPENCE: *J. Am. Chem. Soc.* **51**, 3353 (1929).
- (13) KRAUZE, NEMTZOV, AND SOSKINA: *Compt. rend. acad. sci. U. R. S. S.* **2**, 301-306 (1934); *Brit. Chem. Abstracts* **1934**, 736.
- (14) LEBEDEV: *J. Russ. Phys. Chem. Soc.* **45**, 1249 (1913); *J. Chem. Soc.* **104**, I, 1285 (1913); *Chem. Abstracts* **8**, 320 (1914); **9**, 799 (1915).
- (15) MERESHKOWSKI: *J. Russ. Phys. Chem. Soc.* **45**, 1940 (1913); *Chem. Zentr.* **85**, 1813 (1914).
- (16) MEINERT AND HURD: *J. Am. Chem. Soc.* **52**, 4540 (1930).
- (17) NORRIS: *J. Chem. Education* **9**, 1890 (1932).
- (18) NORRIS AND REUTER: *J. Am. Chem. Soc.* **49**, 2624 (1927).
- (19) NORRIS AND STANDLEY: Paper presented at the Eighty-third Meeting of the American Chemical Society, held in New Orleans, April, 1932.
- (20) NORRIS AND THOMPSON: *J. Am. Chem. Soc.* **53**, 3108 (1931).
- (21) PEASE: *J. Am. Chem. Soc.* **50**, 1779 (1928).
- (22) PEASE: *J. Am. Chem. Soc.* **52**, 1158 (1930); cf. PEASE AND CHESEBRO: *Proc. Nat. Acad. Sci.* **14**, 472 (1928).
- (23) RICE: *J. Am. Chem. Soc.* **53**, 1959 (1931); **55**, 3035 (1933).
- (24) SCHMIDT: *Z. physik. Chem.* **159A**, 337 (1932).
- (25) SULLIVAN, RUTHRUFF, AND KUENTZEL: *Ind. Eng. Chem.* **27**, 1072 (1935).
- (26) TROPSCH AND EGLOFF: *Ind. Eng. Chem.* **27**, 1063 (1935).
- (27) TROPSCH, PARRISH, AND EGLOFF: *Ind. Eng. Chem.* **28**, 581 (1936).
- (28) TROPSCH, THOMAS, AND EGLOFF: *Ind. Eng. Chem.* **28**, 324 (1936).
- (29) VAUGHAN: *J. Am. Chem. Soc.* **54**, 3863 (1932).
- (30) WHEELER AND WOOD: *J. Chem. Soc.* **1930**, 1819.
- (31) WHITBY AND GALLEY: *Can. J. Research* **6**, 280 (1932).



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Nobel Laureate, 1936

A SYMPOSIUM ON THE DIELECTRIC PROPERTIES OF MATTER¹

INTRODUCTION TO THE SYMPOSIUM

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The development of knowledge in all branches of physical, analytical, and inorganic chemistry has been so rapid in recent years that it is difficult for any individual to keep in touch with the advances in the fields outside his own specialty. With the desire to perform a service to its members and to chemistry, the Division of Physical and Inorganic Chemistry of the American Chemical Society has taken upon itself the organization of symposia whose purpose is the correlation of the advances of research in the several fields of its scope and the provision of authoritative and critical summaries of those subjects which have had at the same time consistent and rational development and far-reaching consequences. On this occasion we seek to coordinate the knowledge which has become available on the subject of the dielectric properties of matter. Enough of a theoretical background is given so that the reports to follow may serve as a stimulus for investigators and investigations in this important field. Further, it is hoped that useful conclusions have been reached which may prove of value to scientists and engineers confronted with some practical problem.

The first attempt to describe the dielectric constant as an atomic or molecular property is found in the classical theory of Clausius-Mosotti, according to which the volume actually occupied by the molecules is related in a simple way to this constant. The molecules were considered as conducting spheres, and it is not surprising that it has been necessary to modify the Clausius-Mosotti statements by the electron theory and by the dipole theory of dielectric behavior.

The electron theory considers the molecules in a dielectric to be neutral systems of positive and negative electricity, which are bound by quasi-elastic forces with the center of the positive charges at the same point

¹ Held by the Division of Physical and Inorganic Chemistry at the Ninety-second Meeting of the American Chemical Society in Pittsburgh, Pennsylvania, September, 1936.

within the molecule as the center of the negative charges. If such a molecule is brought into an electrical field it is polarized, and the molecule contains an induced electric moment. Dielectric constant at zero frequency ϵ and molar polarization P can be shown to be related by the same formula which has come to be known as that of Clausius-Mosotti, that is,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4\pi}{3} N\alpha$$

In this formula α is the molecular polarizability, or the electric moment induced by a field of unit strength, and the other symbols have their usual significance.

According to this formula the molar polarization ought to be independent of density and of temperature. If the dielectric constants of gases or vapors are measured at constant density, it is found that for some gases the molar polarization is really constant, but in other cases it decreases with increasing temperature. The substances of the second kind or class have high dielectric constants and low refractive indices, the Maxwell equation $\epsilon = n^2$ is not obeyed, and the molar refraction is smaller than the molar polarization.

In proposing what has now come to be known as the dipole theory Debye (2), in an article published in 1912, modified the Clausius-Mosotti law in such a way as to give an explanation of this and other difficulties. The assumption was made that although the molecule is uncharged, the center of the positive charges may not be at the same point as the center of the negative charges. If this occurs the molecule has a permanent moment, and now can show a polarization not only by electron and atom displacements or distortion, but also by orientation in the electrical field. Furthermore, it may be expected that the amount of orientation created by the field will be larger the smaller the disturbance due to temperature motion. Debye went on to establish the quantitative law for the dependence of orientation with temperature, so that it became possible to obtain the absolute value of the electric moment of gases and properly dissolved molecules from a measurement of the temperature variation of the dielectric constant and density in such systems. This quantitative law takes the form,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \left(\alpha + \frac{\mu^2}{3kT} \right) = A + \frac{B}{T}$$

in which μ is the electric moment of the molecule. According to it the molar polarization is made up of two parts, one due to electron and atom displacement which is independent of temperature, and another resulting

from the orientation of the permanent moment which is a function of the temperature. The formula will be correct insofar as we can represent the energy of the molecule in an electrical field as a function of no higher than the second degree in the field components and can consider only the most important part of the mean electric moment which is proportional to the field of electric intensity.

An immediate consequence of the new theory was the explanation of the anomalous dispersion or decrease of the dielectric constant with increase in frequency first observed by Drude (4) for liquids in which, as was inferred, the molecules contain special atomic groups like OH and NH_2 . Debye (3) reasoned it to be probable that the characteristic property of the liquids with anomalous dispersion in the radio-frequency range is the polarity of their molecules, and that the effect represents the transition of the combined orientation and distortion to a pure distortion of the molecules. A quantitative description of the frequency variation of dielectric constant in liquids was here given.

Now, almost twenty-five years later, we know the modified Clausius-Mosotti equation which describes both temperature and frequency variation to be entirely consistent with the latest quantum theory, and, except in a few special cases, to be fully substantiated by experiment. For reasons not apparent these explanations of temperature and frequency dependence of dielectric constant did not become immediately and widely known. But about a decade ago attention was again called to them, this time in two monumental works, an article in the fifth volume of the Marx *Handbuch der Radiologie* and a monograph, *Polar Molecules*, both written by Debye; at the present time the scope of the subject has been greatly broadened and many important and unique applications have been made to problems of chemistry, physics, and electrical engineering. Because we believe an acquaintance with and a study of this subject to be of value to members of this Division, we have arranged a program to indicate some of the many and varied uses to which the dipole theory has been and will be put in the solution of chemical problems.

Our study may be divided in several ways. We propose here to consider at the same time the actual dielectric behavior of gases, liquids, and solids; electrolyte, non-electrolyte, and dipolar ion solutions; and the application of these ideas to give information about other properties of the several systems. In the arrangements the breadth of the subject has proved a source of considerable difficulty, and it is only to avoid congestion of the program that other important contributions to the subject have been omitted. Especially deserving of mention are recent contributions of Fuoss and Kraus and of Onsager.

In the opening paper Debye gives an account of his recent important

work having to do with the properties of pure liquids. It is pointed out that while there remain no essential difficulties in describing the dielectric behavior of gases, the theory developed can not be applied to pure liquids without considerable modification. Binding forces between molecules become of such significance that molecular rotation is restricted and the liquid assumes a quasi-crystalline character. The successful calculation of this binding energy is a large factor in bringing the theory abreast with the rapid progress which has been made in experimental researches having to do with effects of electrical saturation, anomalous dispersion, electric double refraction, interference maxima in the scattering of x-rays, association, specific heat, and other properties, all in the liquid state.

Many of the configurations of which molecules are constituted are strongly polar in character. In the compounds of organic chemistry the dipole moment of these groups proves to be largely independent of the length of the non-polar hydrocarbon chain to which they are attached. The moments of the groups are additive as vectors, with the result depending upon the configuration of the molecule. Thus once more a physical chemical theory finds important application and utility in the chemistry of organic compounds. The Division is fortunate in having a distinguished English chemist, N. V. Sidgwick, to consider in detail the relationship between electric moment and molecular structure. This application of the Debye dipole theory to problems of molecular configuration was early recognized, thoroughly understood, and skillfully used by him.

The available data for the dielectric constants of gases at higher densities are of interest in the theory of dielectrics. Keyes and Oncley show that the results of most investigators are in agreement with the observation that the polarizability of compressed gases may increase by several per cent in some cases, although the simpler gases show little, if any, change. The origin of this increase in polarizability and its significance to the theory of dielectrics and problems involving the molecular field are discussed.

The electric moments of molecules are estimated usually either in the gaseous state or in non-polar solvents. With the contribution of Debye contained in this volume as an aid, we can look forward to the time when molecular behavior in polar solvents will be described, but until now there is no completely satisfactory theory for such polar solutions. In spite of this fact experimental research has made rapid strides, and certain important relationships have been made apparent between the polarity of molecules and the dielectric constants of these solutions. In this field the work of Wyman has been outstanding. He summarizes here the various

methods which can be used, and presents data which reveal great regularity and simplicity of behavior.

The amino acids and proteins are constituted of a relatively small number of chemical groups. Recognition of this fact and the realization of its significance has enabled Cohn to point the way in one of the most active fields of research in all biochemistry. In clear and lucid fashion we are shown that the electrostatic forces in biological systems must be considered to involve not only ions but also the dipolar ions. Here, then, the activity coefficients reflect not only Coulomb forces but also the space properties both of ions and of dipolar ions. Since electrostatic forces surrounding ions are of longer range than those surrounding dipolar ions, whereas the latter are larger and contain an appreciable proportion of non-polar groups, interaction between ions, between ions and dipolar ions, and between various dipolar ions reflects such forces as the so-called "salting-out effect" the more, the larger the volume of the dipolar ion in comparison with its electrical moments and the greater the dielectric constant of the solvent. These effects are therefore being studied at high dielectric constants in systems containing many components.

In chemistry the extraordinary importance of solubility is universally recognized. Much of the recent progress made in solution theory has resulted because investigators have learned how to take into account the polarization, dispersion, and repulsive forces between the ions, and the forces of interaction between ions and solvent molecules, and between different solvent molecules. In short, the foundation of a general theory of intermolecular forces has been laid.

The two contributions which follow are concerned with solubility problems. In the first of these, Kirkwood treats the statistical mechanics of liquids and liquid solutions in convincing fashion. Relations between the more important thermodynamic functions of fluids, and the potentials of intermolecular force are formulated in terms of the probability distribution function of molecular pairs. The potential of average force, which determines the distribution of pairs, satisfies an integral equation, which has been solved in certain cases. Special attention is devoted in one of the chapters of this article to a consideration of the nature of the Debye-Hückel method and its application to electrolytes and to mixtures of electrolytes and dipole ions. The treatment shows Debye's theory to be a direct, proper, and logical consequence of statistical laws; at the same time it suggests the ways for its elaboration in more complicated systems.

Numerous investigators have attempted to treat theoretically the properties of concentrated solutions of strong electrolytes. Profound knowledge of the statistical mechanics of solutions and long continued

effort have enabled Scatchard to make contributions of importance to this difficult subject. In the present instance it is shown that if the dielectric constant appearing in the Debye electrolyte theory behaves like that of a polar-non-polar mixture, the thickness of the ion atmosphere is proportional to the square root of the volume of the solvent. The chemical potentials in aqueous alkali halide solutions now may be calculated from the radii of the ions and two other parameters. Where more complex ions are involved much progress is made by the application of a general theorem of statistical mechanics, the Debye-Hückel limiting law, and an extension of the Brönsted principle of specific ion interaction.

In his theory of the frequency behavior of the dielectric constant, we have seen that Debye could explain the anomalous dispersion in liquids known since the experimental work of Drude. A problem now attracting much attention has to do with anomalous dispersion effects in certain crystalline solids and its theoretical explanation. In his admirable review of the dielectric constants of solids, Smyth points out that the molecules of some solids possess freedom to turn in an electrical field so as to orient their dipoles in the field and give a high dielectric constant, like that of a polar liquid. In ionic solids the dielectric constant is high because the displacement of ions in a field occurs more readily than that of electrons bound in a molecule, but in molecular solids the shift of charge is mainly a displacement of electrons and the susceptibility is low.

Pioneer work of Brönsted (1) dealing with the effect of the concentration of electrolyte upon reaction rate, has given new impetus to the study of the effect of acids and bases in catalyzing certain reactions. With this work as guiding principle, exact kinetic data for such reactions as the decomposition of nitramide, the inversion of sucrose, and the mutarotation of glucose have received ready interpretation. In the report which forms the last article of the proceedings, La Mer describes studies of these reactions in deuterium oxide, which lead him to conclude that the kinetic effects are primarily the result of displacements in the exchange equilibria between proto and deuterio forms of the substrate or of the catalyst. The importance of exchange reactions in solution is demonstrated as well in the case of certain electromotive force studies. Conductance change as solvent is varied from ordinary water to deuterium oxide is determined by the viscosity difference.

The consummate skill with which Debye was able with his dipole theory to remove the difficulties of the Clausius-Mosotti and electron theories, and to explain the anomalous dispersion effects, constitutes one of the most brilliant achievements in all physical chemistry. In printed article and by personal association he has suggested applications of this theory which have

meant much in the development of modern physical and organic chemistry. We consider it fitting, then, that we dedicate to him this printed record of the proceedings of the symposium.

REFERENCES

- (1) BRÖNSTED: Z. physik. Chem. **102**, 169 (1922); **115**, 337 (1925).
- (2) DEBYE: Physik. Z. **13**, 97 (1912).
- (3) DEBYE: Verhandl. deut. physik. Ges. **15**, 777 (1913).
- (4) DRUDE: Z. physik. Chem. **23**, 267 (1897).

DIELECTRIC PROPERTIES OF PURE LIQUIDS¹

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1. There are now no essential difficulties in understanding the dielectric properties of gases at sufficiently low pressures, if one takes into account the fact that the molecules are not only polarizable but can also be oriented because of the existence of a permanent electric dipole. The same situation exists also for dilute solutions of polar molecules in non-polar solvents, if we neglect small corrections arising from the effect of the solvent. The situation is quite different, however, when one tries to understand on the basis of the theory developed for gases the dielectric properties of the common pure liquids in which the molecules approach each other closely. Particularly impressive is this complication in the case of liquids with relatively small, highly polar molecules. However, it must be stressed that the complications are not confined to this particular limiting case. They appear, even if not in such a striking fashion, in the case of all liquids, even the non-polar ones, and clearly have as their origin the mutual influences of the neighboring molecules, which are not necessarily connected with the existence of permanent dipoles.

2. It is clear then that the main problem in the understanding of pure liquids is the interpretation of the mutual interactions between the molecules. A very striking example of these general considerations is water. The molecule H_2O is polar and has a dipole moment equal to 1.84×10^{-18} electrostatic units, according to measurements made with water vapor. This enables one to calculate the molecular orientation-polarization, with the aid of the well-known equation

$$P_0 = \frac{4\pi}{3} N \frac{\mu^2}{3kT} \quad (1)$$

in which N is the Avogadro number, μ is the moment, k is the Boltzmann constant, and T is the absolute temperature. Thus the theoretical value

¹This paper was also delivered at the Tercentenary Conference of Arts and Sciences at Harvard University, September, 1936.

of P_0 is equal to 71 cc. The experiments with liquid water give, however, a dielectric constant $\epsilon = 81$, and from this, using the equation

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} \quad (2)$$

one obtains for liquid water the total molecular polarization $P = 17$ cc. In this equation M is the molecular weight and d is the density. Part of this value is to be ascribed to the polarizability of the molecules and not to their orientations. This amounts, as one knows from the optical refractive index measurements, to about 4 cc. Hence in contrast to the calculated value $P_0 = 71$ cc., one obtains from the experiments for the liquid only $P_0 = 13$ cc. as the orientation-polarization. One cannot believe that the dielectric properties of a water molecule can be influenced to such an extent by the close proximity of the other molecules. It is much more natural to believe that in the liquid the orientation of a molecule is influenced by its neighbors while measurements in the electric field are being made. Accordingly, equation 1, which presupposes completely free rotation, should not be applied to liquids without large corrections. A very beautiful example of how such corrections become of practical importance when the molecules approach each other is to be found in the measurements of the dielectric constant of sulfur dioxide at high densities by Everheim (1902). At a temperature of 150°C. and a density of $\delta = 0.76$ g. per cubic centimeter a value $P_0 = 33$ cc. is found for the orientation-polarization, whereas from the known dipole data one calculates $P_0 = 37$ cc. Here the two values are still quite close together. However, at a temperature of 14.5°C. and a density of $\delta = 1.39$ g. per cubic centimeter the value $P_0 = 27$ cc. is obtained, while the theoretical value is $P_0 = 55$ cc.

A study of the electric double refraction (Kerr effect) shows very clearly that also in the case of non-polar liquids the free rotation is considerably inhibited, as has been mentioned before. As an example of such molecules we mention carbon disulfide. From measurements of the electric double refraction in the vapor phase one calculates for the three polarizabilities of the molecule, $\alpha_1 = 15.1 \times 10^{-24}$ in the direction of the S—C—S molecular axis and $\alpha_2 = \alpha_3 = 5.54 \times 10^{-24}$ in the directions perpendicular to the molecular axis. From these data one calculates for the Kerr constant of the liquid, according to the equation

$$\frac{n_p - n_s}{n_0} = K \mathcal{E}^2 \quad (3)$$

the value $K = 19.7 \times 10^{-12}$. In the equation n_p is the refractive index parallel to the field, n_s is the refractive index perpendicular to the field,

n_s is the normal refractive index, and \mathcal{E} is the field strength in electrostatic units. Direct measurements with the liquid give instead a value 40 per cent lower, namely $K = 11.8 \times 10^{-12}$. Nevertheless, the average polarizability of the molecule, $\alpha = \frac{1}{3} (\alpha_1 + \alpha_2 + \alpha_3)$, is not affected by the change to the liquid state, as one can conclude from the comparison of the refractive indices of the gas and the liquid using the Lorenz-Lorentz equation. One has, therefore, the alternative either of assuming that the differences in the polarizabilities of the molecule in different directions have been decreased on a change to the liquid state, while their sum remains unchanged, or that in the liquid the molecule is no longer free to orient itself in the external field as it is in the gas. Obviously the second alternative is to be selected.

3. Through these preliminary considerations we are led to concentrate our attention on the binding which exists between the molecules in a liquid. Such binding is quite familiar to us from the study of the solid state, where it is responsible for the elastic properties of crystals. From the point of view of the van der Waals continuity between gases and liquids, understanding of these forces is more difficult. However, even from the point of view of the classical theory one can raise the question as to how far the transition to the solid state has been achieved in the liquids. Indeed, within the last few years a variety of experiments has demonstrated that one is justified in discussing the quasi-crystalline structure of liquids. After the first joint experiments of the speaker and Scherrer had demonstrated (1916) that one obtains interference maxima in the scattering of x-rays by liquids, many experiments of other investigators, among which should be mentioned the studies of Keesom on liquefied gases and the extended and beautiful investigations of Stewart (Iowa), have clearly interpreted the origin of the main interference maxima. There must exist in the liquids small regions of space within which the relative orientation of molecules approximates very nearly the perfectly regular arrangement in the solid cluster, the only difference between the two being that in liquids this orientation depends on time. A particularly clear understanding of the situation is obtained from the study of the scattering of x-rays by monatomic liquids, as, for instance, mercury. Where the single atoms give an intensity of scattered rays which monotonously decreases with increasing angle between the primary and the secondary ray, the same atom present as a liquid produces very noticeable interference maxima and minima. In this particular case it is even possible to determine the mutual orientation and the preferred distances between the atoms from a probability curve to be deduced from the scattering measurements. It thus becomes clear that in molecular orientation the liquids behave as quasi-crystals.

As the experiments with the scattering of light of ordinary frequencies

demonstrate, there exists a similarity between the liquids and the crystals not only in the orientation but also in the types of allowed molecular motions. If one studies monochromatic light scattered by a liquid with the aid of an apparatus with high resolving power, such as an echelon-grating, one finds that the originally monochromatic line has been split into a narrow triplet due to the process of scattering. The magnitude of the separation of the triplet components depends on the direction at which the observation is made, and is the greatest at a scattering angle of 180° . The central line of the triplet has the same frequency as the original light. The separation of the two exterior symmetric components of the triplet is the larger, the higher the sound velocity in the liquid. These facts, which have been established in experiments of Gross, Meyer, Raman, and others, would be entirely incomprehensible if the molecules in the liquid had freedom of motion independently of each other. In that case the molecular motions would produce not a splitting of the original line into a triplet but merely a broadening of it. We know that in an ideal solid body the motions of an atom are to be understood as superposition of motions which produce a very large number of thermal sound waves which are propagated through the body in all directions. The correctness of the T^3 law for the specific heat of solid bodies at low temperatures is the experimental proof of this. L. Brillouin has investigated in a theoretical work the scattering of light in an ideal solid body, and finds that this scattering must be considered as a Bragg reflection by the sound waves and that in consequence of the coöperation of the Doppler effect the primary spectral line must be split into a doublet.

Liquids do not exhibit a broadening but a splitting. From this we conclude, following Brillouin's calculation, that the motions of neighboring molecules are strongly coupled in liquids also, just as in solid bodies. The fact that in addition to the doublet of the Brillouin theory, one observes with liquids the third, unshifted line is obviously to be explained as meaning that a liquid is not an ideal solid body. As is well known even for crystals the ideal solid body is only a limiting case which can never be realized in practice, because it cannot have any heat expansion. Reasoning in this manner Placzek and Landau have recently interpreted, in a short letter to the author, the intensity of the middle component of the scattered light as connected with the difference of heat capacities of liquids at constant pressure and of constant volume. Recent experiments carried out in Leipzig have indeed confirmed this interpretation of the intensity distribution among the three lines of the scattered light. Altogether one can conclude with complete certainty that the orientation and coupling of molecules in liquids are very similar to the binding of molecules in solid crystals.

4. In order to obtain an idea as to the mode of motion of an atom in a monatomic liquid by using the concepts which we have now developed, we make the following statements. The atom is vibrating very much as in a solid crystal, and therefore has on the average approximately the same amount of kinetic as well as potential energy. However, and this is typical of the liquid, the center of vibrations is not stationary but instead moves slowly through the liquid as in Brownian motion. In perfect agreement with this is the observation that the heat capacity of liquid mercury has very nearly the value required by the Dulong-Petit law. Of far greater interest to us is, however, the behavior not of monatomic liquids but of liquids consisting of rather complex molecules. In this case we are much more interested not in translational motions of the center of gravity of a molecule, but in rotations of the molecule. One is tempted to form a picture of this motion which is very similar to that developed for the translations. It should not be considered a free rotation but rather a kind of torsional vibration, the axis of which undergoes a slow rotation in space instead of being rigidly fixed as it is in the case of torsional vibrations in crystals.

When one tries to apply these ideas to the mathematical problem of the dipole orientation in liquids, one concludes that the molecules are influenced in liquids by two kinds of forces. First, the molecule is exposed to the usual couple due to the external electric field; and second, there exists a potential energy which acts to hold the molecule in its instantaneous position fixed by its surroundings. For this potential energy one can assume as the very simplest approximation an expression of the form

$$u = - E \cos \theta \quad (4)$$

where θ is the angle between the axis of the permanent electric moment and the instantaneous axis fixed by the surroundings. It is quite obvious that an equation of the form 4 is not capable of representing the detailed behavior in all special cases. However, one can regard equation 4 as the first term in a series of spherical harmonics, and hope that even this first term is a good approximation to reality. The total energy of a dipole in a field F is to be obtained by adding to the energy given by equation 4 also the field energy $-\mu F \cos \theta'$, where θ' is the angle between the dipole axis and the external field. One can readily calculate the average component of the dipole in the direction of the field F . However, this will depend to a great extent on the angle between the field and the axis, which is fixed by the surroundings of the molecule. The final average observable moment in the direction of F is then to be obtained by averaging over all such orientations caused by the molecular surroundings. The quantitative expression representing this average moment in the direction of F is given by

$$m = \frac{\mu^2}{3} \frac{E}{kT} [1 - L^2(\beta)] \quad (5)$$

in which β is an abbreviation for $\beta = \frac{E}{kT}$, and L is the well-known function of Langevin so useful in the theory of magnetization, namely

$$L(\beta) = \coth \beta - \frac{1}{\beta} \quad (5')$$

Equation 5 shows, according to our expectations, that the interactions between the molecules of a liquid interfere with the orientation of the dipoles in an external field. The classical value

$$m = \frac{\mu^2 F}{3kT}$$

which one obtains for the completely freely rotating molecules, is now to be multiplied by a factor $[1 - L^2(\beta)]$, less than unity. In the case of small binding forces ($E \ll kT$) this factor is very nearly unity, and in the cases of large binding forces ($E \gg kT$) it tends towards the value

$$\frac{2}{\beta} = \frac{2kT}{E}$$

which it reaches for very large values of binding energy E , so that then the effect of permanent dipoles is completely eliminated. One can estimate this factor as equal to unity less the ratio of the value of the average moment in the direction of the instantaneous axis in the absence of the external field to the absolute value of the moment. It is most noteworthy that this result holds irrespective of the special assumptions involved in defining equation 4, and is valid for any arbitrary law of force.

Let us now consider the applications of equation 5 and start by considering the case of water. The experimentally determined molecular orientation polarizability was 13 cc., whereas the theoretically calculated one for the case of freely rotating molecules is 71 cc. Thus the experimental reduction factor is $13/71 = 2/11$. According to the above theory this reduction factor for the case of strong binding forces, which are obviously present here, is equal to $2/\beta$. We will obtain an agreement with experiment, therefore, if we assign to the binding energy in liquid water, in agreement with the definition of β , the value $E = 11 kT$. This is an extremely large value; it produces a hindering of orientation such as would be produced by a field of some 72,000,000 volts per centimeter. From a molecular point of view, however, this magnitude of energy is quite understandable, since a

field strength of 72,000,000 volts per centimeter would be produced by a water dipole at a distance of 2.5×10^{-8} cm. Approximately the same value of E is observed for instance in the case of nitrobenzene, whereas for the liquid diethyl ether the reduction factor is almost unity, so that E is almost equal to zero and the molecules must have an almost free rotation. In between these extremes are to be found the alcohols. Thus for ethyl alcohol the reduction factor is 0.56, which means, according to equations 5 and 5', that the binding energy is $E = 2.9 kT$. With increasing length of the carbon chain in alcohols this binding energy decreases.

5. The preceding estimates indicate that the magnitude of the binding energy E is an excellent measure of the extent of that type of association in liquids which affects the orientation. The representation of the binding energy through an equation as simple as equation 4 and the use made of it in the following calculations is, of course, to be regarded as the first rather crude approximation to reality. In this connection it becomes of considerable interest to see how far this representation is capable of explaining other, thus far not considered, properties of liquids. A phenomenon which is very characteristic of the dipole orientation is the decrease in dielectric constant observed with a strong external field. It is particularly in the case of the saturation that enormous differences between theory and experiment are to be observed with associated liquids. The first accurate measurements of the saturation effect were made on ethyl ether by Herweg. His measurements corrected for electric double refraction and electrostriction were discussed by means of a formula derived from the dipole theory adapted to molecules with free rotation. It was

$$\epsilon = \epsilon_0 - \frac{4\pi}{15} n \frac{\mu^4}{k^3 T^3} \left(\frac{\epsilon_0 + 2}{3} \right)^4 \mathcal{E}^2 \quad (6)$$

In this formula ϵ is the dielectric constant measured in the field \mathcal{E} and n is the number of molecules per cubic centimeter in the liquid. For ethyl ether, the only substance used in his experiments, there was perfect agreement between theory and experiment. Later on Malsch thought that the experiment would be easier working with liquids of high dielectric constant, for in this case the inner field strength is greater than the external field strength by the factor

$$\frac{\epsilon_0 + 2}{3}$$

There were some difficulties, derived from the fact that all liquids with high dielectric constants are conducting, but these difficulties were overcome by a special method. The results of the experiment were in com-

plete disagreement with the theory. Thus, for instance, one obtains from equation 6 that for water

$$\frac{\epsilon - \epsilon_0}{\epsilon_0} = -3.9 \left(\frac{\mathcal{E}_v}{100,000} \right)^2$$

if the external field strength \mathcal{E}_v is measured in volts per centimeter. On the contrary, the experimental results gave

$$\frac{\epsilon - \epsilon_0}{\epsilon_0} = -1.1 \times 10^{-3} \left(\frac{\mathcal{E}_v}{100,000} \right)^2$$

It is seen that for water the experimental effect is 3500 times smaller than that calculated. In other cases similar, although not so enormous, differences occur; thus for instance in the case of ethyl alcohol the observed effect is fourteen times smaller than the calculated.

The question arises whether these differences can be understood as a result of the quasi-crystalline structure of the liquids and whether they can be explained quantitatively with the help of our former assumptions. By assuming for the binding energy the same formula as before, i.e., $u = -E \cos \theta$, and by calculating the orientation-polarization to a higher approximation, the result is that in equation 6 the second member has to be multiplied by a reduction factor R . This factor can be represented by the formula

$$R(\beta) = 3 \left[(1 - 4L^2 + 3L^4) + 4 \frac{L}{\beta} (2L^2 - 1) + 6 \frac{L^2}{\beta^2} \right] \quad (7)$$

in which again L represents Langevin's function. For large values of $\beta = E/kT$, R is given by

$$R(\beta) = 3/\beta^4 \quad (7)$$

Now if for water Malsch's results are adopted, $3/\beta^4 = 1/3500$ and $\beta = 10$, that is to say $E = 10 kT$. This means that the same binding energy which had to be assumed to understand the value of the orientation-polarization, which is 5.5 times smaller than the calculated value, explains at the same time why the saturation effect is found experimentally to be 3500 times smaller than the one calculated. It is true that a small difference exists, in that $E = 11 kT$ has been derived from the orientation-polarization, whereas in this case $E = 10 kT$ is found, but this difference is within the experimental error of the Malsch measurements. The results found in the cases of ethyl alcohol and ethyl ether are also satisfactory. In the first case, in which the saturation effect has been found to be fourteen times smaller than that calculated, it follows that $\beta = 2.9$. This is

in accordance with the value derived for β from the orientation-polarization. In the second case we know that the orientation-polarization nearly equals the value calculated for free molecules and we understand, therefore, why Herweg could represent his experimental results by means of equation 6 without introducing any reduction factor at all.

6. Another phenomenon which is characteristic of substances with polar molecules is the anomalous dispersion and absorption in the range of long electric waves, which was discovered by Drude. The theory, which so far has only been applied to the case of free dipoles, gives an explanation of this effect by stating that at high frequencies a phase difference exists between the electric field and the dipole orientation. This can be expressed formally by an equation giving the average moment m in a field of the strength $Fe^{i\omega t}$ as follows:

$$m = \frac{\mu^2}{3kT} \frac{Fe^{i\omega t}}{1 + \frac{i\rho\omega}{2kT}} \quad (8)$$

The constant ρ of this formula is a measure of the friction opposing rotation, and if the molecule is represented by a sphere of the radius a , and if η is the coefficient of viscosity of the liquid,

$$\rho = 8\pi\eta a^3 \quad (8')$$

In this way we not only express that the dispersion and absorption effect is limited to the case of polar liquids, but also that the frequency at which these effects occur is intimately connected with the viscosity of the liquid. Many observers have made experiments which indicate that this connection between viscosity and frequency is qualitatively correct, but in certain cases it was necessary to introduce a molecular radius, a , smaller than the value known to be correct. A very characteristic example of such a case is glycerin. It can be said that for particles of molecular dimensions we have no experience as to their frictional constants and that it is not impossible that in such a case Stokes' formula, containing the ordinary viscosity constant, does not hold. On the other hand, it is not to be forgotten that the temperature variation of the dispersion and absorption effect is closely related to the temperature variation of the viscosity. From this point of view it seems interesting to calculate how much the theoretical result will be influenced by the fact that the molecules are not free but that we have to deal with a quasi-crystalline structure.

The calculations are much more complicated than those we had to deal with; it will be sufficient here to give only the main outline. An equation has to be found for the distribution function f of the dipole axis, the latter

being at the same time under the influence of the molecular binding energy u_0 , and the variable field $F e^{i\omega t}$ causing an energy of orientation

$$u_1 = -\mu F e^{i\omega t} \cos \theta'$$

As in the case of free dipoles an equation for Brownian motion of rotation can be used. If, moreover, the effect is taken into account, the external field can only create a very small orientation effect, and the problem can be formulated as follows.

If the total energy of a dipole as it is influenced by its surroundings and by the electrical field can be represented by

$$u = u_0 + u_1 e^{i\omega t}$$

and if we assume

$$f = f_0 + f_1 e^{i\omega t}$$

we obtain

$$f_0 = C \cdot e^{-\frac{u_0}{kT}}$$

and the function f_1 is found as a solution of the equation

$$\begin{aligned} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \left[\frac{\partial f_1}{\partial \theta} + \frac{f_1}{kT} \frac{\partial u_0}{\partial \theta} \right] + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left[\frac{\partial f_1}{\partial \phi} + \frac{f_1}{kT} \frac{\partial u_0}{\partial \phi} \right] - \frac{i\omega \rho}{kT} f_1 \\ = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \left[\frac{f_0}{kT} \frac{\partial u_1}{\partial \theta} \right] - \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left[\frac{f_0}{kT} \frac{\partial u_1}{\partial \phi} \right] \end{aligned} \quad (9)$$

in which θ and ϕ are the ordinary spherical coördinates.

The solution of the problem can be represented in the following way. Starting with the equation,

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \left[\frac{\partial X_n}{\partial \theta} + \frac{X_n}{kT} \frac{\partial u_0}{\partial \theta} \right] + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left[\frac{\partial X_n}{\partial \phi} + \frac{X_n}{kT} \frac{\partial u_0}{\partial \phi} \right] + \lambda_n X_n = 0 \quad (10)$$

one has to find first of all such values of λ_n that the functions X_n can be considered as eigenfunctions on the sphere. Thus we have obtained a generalization of the ordinary spherical harmonics which represent the X_n for $u_0 = 0$ with $\lambda_n = n(n+1)$. If then these functions are known, the right-hand term in equation 9 can be represented by an expansion in series of the form

$$\sum c_n X_n$$

and we find

$$f_1 = \sum \frac{c_n X_n}{\lambda_n + \frac{i\omega\rho}{kT}}$$

This is the way that was followed, assuming equation 4 for the binding energy. However, it was only possible to represent the functions by expanding them in powers of

$$\beta = \frac{E}{kT}$$

For small values of β , and at the same time for small values of $\omega\rho/kT$, the average moment, m , is given by the expression

$$m = \frac{\mu^2 F e^{i\omega t}}{3kT} \left[\left(1 - \frac{\beta^2}{9} \right) - \frac{i\omega\rho}{2kT} \left(1 - \frac{11}{54} \beta^2 \right) \right] \quad (12)$$

For large values of β calculations are much simpler, because in this case the motion of the dipole can be approximated by a simple vibration about an axis defined by the interaction of the surrounding molecules. In this limiting case the result is

$$m = \frac{\mu^2 F e^{i\omega t}}{3kT} \cdot \frac{1}{\frac{\beta}{2} + \frac{i\rho\omega}{2kT}} \quad (12')$$

It is very simple to judge the results to be drawn from these formulas for the limiting cases $\beta = 0$ and $\beta \gg 1$. If they are represented as in

$$m = \frac{\mu^2 F e^{i\omega t}/3kT}{1 + \frac{i\rho\omega}{2kT}} (\beta = 0); \quad m = \frac{\mu^2 F e^{i\omega t} / 3 \frac{E}{2}}{1 + \frac{i\rho\omega}{2 \frac{E}{2}}} (\beta \gg 1) \quad (12'')$$

it is seen that the transition from the case of that of free dipoles to strongly bound dipoles can be performed by replacing the thermal energy kT by the much larger energy $E/2$. It follows then from the formulas for the dielectric losses and for the dispersion effect that we have at the same time a diminution of the dipole action to be observed both in the dielectric constant itself and in the losses. The binding energy is acting (in the case of large values of β) just as if the constant

$$\rho = 8\pi\eta a^3$$

had been diminished, and this can be interpreted by saying either that the viscosity is less than normal or that the molecular radius is smaller than would be expected. Further experiments are still necessary, but the fact that the greatest differences between experiment and theory occur for highly associated liquids makes it probable that also in this case the difficulties will be overcome by taking account of their quasi-crystalline structure.

DIPOLE MOMENT AND MOLECULAR STRUCTURE

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This subject is practically the growth of the last eight years. Several of us remember the eagerness with which we learned, at the meeting of the Bunsen Gesellschaft in Munich in 1928, what the moments of a few of the most familiar molecules were; we now know those of some twelve or fifteen hundred compounds.

The methods of measurement usually employed are well known; most of them depend on the determination of the molecular polarization of the substance, either as a gas or in dilute solution in a non-polar solvent; the electronic (and to a certain extent the atomic) polarization is eliminated by making the measurements over a considerable range of temperature, or by observing the refractivity in the visible, or sometimes by measuring the dielectric constant of the substance in the solid state. There are also one or two methods of an entirely different kind, which are of value in particular cases, as well as being important in confirming the general theory. The best known of these is the "molecular beam" method (41, 5; see also 8), an adaptation of the famous Stern and Gerlach experiments for the determination of the magnetic moments of atoms. In this a thin ribbon of molecules at very low pressure is passed through a highly inhomogeneous electric field, and from the observed spreading of the beam an approximate value of the dipole moment can be obtained. A still more recent and as yet little developed method is that depending on the determination of the dielectric losses, that is, of the energy lost as heat when the substance is exposed to a rapidly alternating electric field (3).

The investigation of the dipole moment in its relation to the structure, like that of all new physical properties, has been passing through two stages, the first more or less qualitative, and the second quantitative. There was a whole series of structural problems in which the moments of the alternative structures differed so widely that a rough measurement of the moment was enough to decide between them. The extreme cases were where one of the alternative formulas was polar and the other non-polar. In many of these the conclusions derived from the dipole measurements have been confirmed and extended by other methods, such as those depending on

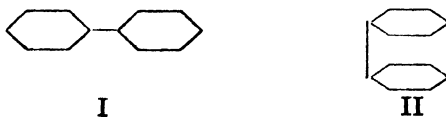
the absorption spectra and the crystal structures, but the dipole method was among the earliest to give us the information we needed. Examples of various structures established in this way are the following: symmetrical (not pyramidal), methane, carbon tetrachloride, and the XCl_4 compounds in general; plane, bismuth trichloride; pyramidal, ammonia, phosphine, phosphorus trichloride; linear, carbon dioxide, carbon disulfide; triangular, water, sulfur dioxide.

Then there were a variety of more special types of molecules, where the alternative structures that were chemically possible, though both polar, differed markedly in moment. Of fundamental importance here were the halogen hydrides—hydrogen chloride, hydrogen bromide, and hydrogen iodide—with the moments 1.03, 0.78, and 0.38 D , respectively (42), because of the light they threw on the distinction between covalent and electrovalent links. The distance between the atomic nuclei in gaseous hydrogen chloride has been shown to be 1.273 A.U. Hence if the molecule is ionized, and the charges can be regarded as located on the nuclei, its moment should be $4.77 \times 1.273 = 6.1 D$. The actual value is 1.03 D , which is only 17 per cent of this. If the binding pair of electrons in $\text{H}-\text{Cl}$ could be regarded as equally shared between the atoms the moment would of course be zero. It is thus evident that though the condition of the molecule is in some sense intermediate between the two extremes, it comes much nearer to the covalent state. This conclusion is supported by the observed values for other covalent links which are of the same order of magnitude, and also by the observation of Wrede (41) that the moments of true salts, such as the alkaline halides, in the gaseous state are much larger, and of the order of 10 D , their theoretical value for complete ionization being between 10 and 20 D .

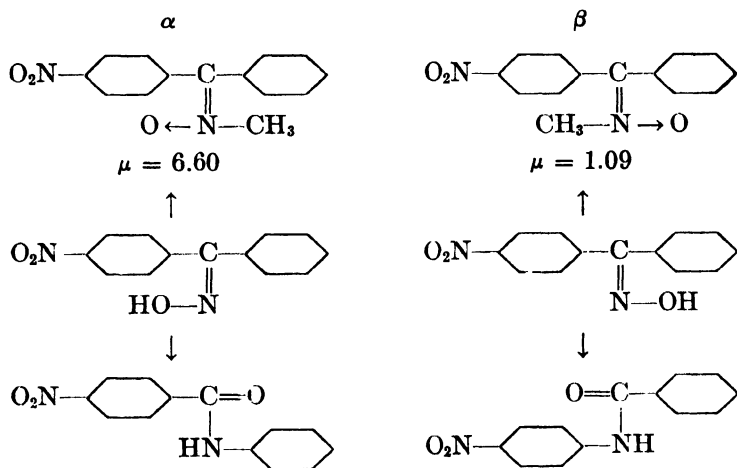
The dipole evidence was also able to solve a variety of other problems of a less general kind: (1) The correct structures of the dihalogen substitution products of ethylene



could be assigned as soon as the moments had been measured, and this was done by Errera (4). (2) In the same way the *trans*-configuration of azobenzene was definitely proved by showing that it is non-polar (2). (3) The formula (II)

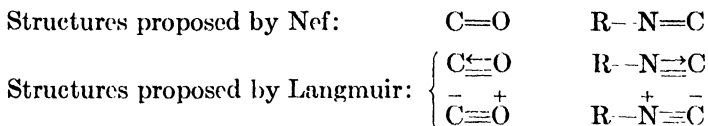


proposed by Kaufler for diphenyl was shown by the work of Williams, Weissberger, and Sängewald (40, 35, 38) to be impossible. They showed that the moments of the *p,p'*-derivatives are practically identical with those of the *p*-disubstituted benzenes having the same substituents; where the moment of the substituent group is symmetrical to the central line of the molecule the compound is non-polar, otherwise it is polar. It follows that the Kaufler formula must be given up, and that the two phenyl groups lie in the same plane (formula I). (4) The controversy as to the structures of the isomeric oximes, between the original Hantzsch-Werner view and that of Meisenheimer, was finally settled in favor of the latter by the measurement of the moments of the oxime ethers. Taylor and Sutton (33) showed, for example, that the isomeric α - and β -*N*-methyl ethers of *p*-nitrobenzophenone had moments of 6.60 and 1.09 *D*, respectively; this made it clear that in the former the highly polar —NO_2 and $\text{N}\rightarrow\text{O}$ groups were acting in the same direction, while in the latter they were opposed to one another. Since the former ether is obtained from the oxime which in the Beckmann reaction is converted into the anilide of *p*-nitrobenzoic acid, it follows that the Beckmann change is a *trans* and not a *cis* migration, and that Meisenheimer's view is correct:

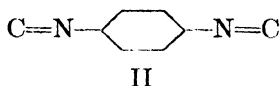
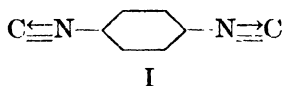


(5) The plane structures of the benzene and naphthalene molecules were established by means of the moments of their derivatives before they had been proved by the crystal structure. For benzene this was implicit in the very ingenious method used by Williams (37) to determine the direction of the moments of groups by balancing them against one another in the para position in benzene; and its truth was shown by his discovery that both the compounds $p\text{-C}_6\text{H}_4\text{X}_2$ and 1, 3, 5- $\text{C}_6\text{H}_3\text{X}_3$ always had approxi-

mately zero moment if the C-X dipoles lay in the direction of the valence joining C to the next atom of the X group. For naphthalene the decisive test is the moment of the 2,6-di derivative (39; for more recent work on the naphthalene derivatives see reference 34). (6) The structure of the divalent carbon compounds, such as carbon monoxide and the isocyanides, was investigated by means of the moments, which entirely confirmed the structures proposed by Langmuir, as opposed to those of Nef (10; see also 20):



The essential points are the minute polarity of carbon monoxide, showing that there has been an electronic transference from the oxygen to the carbon, and in the isocyanides the magnitude and direction of the moment of the $-\text{N}-\text{C}$ group, in which it was shown that the terminal carbon atom is at the negative end of the dipole, which supports the same view. A final test is the observation (30) that *p*-diisocyanobenzene is non-polar; this must be so according to the Langmuir structure (I) but not according to that of Nef (II).



(7) A question arising out of this is the structure of acetylene and its derivatives. Nef maintained that, in particular, diiodoacetylene had not

the obvious linear structure $\text{I}-\text{C} \equiv \text{C}-\text{I}$, but the tautomeric form $\text{C} \equiv \text{C} \begin{array}{l} \nearrow \text{I} \\ \searrow \text{I} \end{array}$.

The former should obviously be non-polar, while the latter should have a considerable moment. The substance was examined, and shown to be non-polar, so that it must have the linear formula (31).

With all these molecules the differences in the moments to be expected on the alternative theories are so large that quite rough determinations of the moments are sufficient to settle the questions at issue.

This stage of the investigations is nearly complete, and all the more obvious plums have been gathered, although we shall always have new problems arising which can be settled in this way. We have now entered on the more advanced and more quantitative branch of the subject, where we endeavor to draw conclusions from small differences of moment. Here we meet with various difficulties, which are essentially of two kinds, the

first being in the accurate measurement of the moments, and the second in their interpretation.

The difficulties of measurement are two, one depending on the allowance to be made for the atomic polarization, and the other on the effect of the solvent.

The atomic polarization for some time afforded a refuge to chemists who found moments that were incompatible with their preconceived ideas; it was always possible to explain them away by the supposition that some of the compounds in question had abnormally large atomic polarizations. Recently this loophole has been fairly well closed. The atomic polarization can be measured by determining the polarization in the gas over a considerable range of temperature, since P_E and P_A are independent of temperature, and so can be separated from P_0 . Another method is to measure the dielectric constant of the solid, in which the orientation of the molecules is fixed, so that the polarization depends on P_E and P_A alone; this may however need some modification in view of the frequent rotation of atomic groups in crystals. The general result of these measurements has been to show that the atomic polarization is never large, and seldom, in molecules of the size with which we are ordinarily concerned, exceeds some 4 cc. or so (24, 26, 12).

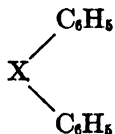
The influence of the solvent on the polarization was first pointed out by Horst Müller (17), who showed that the value of P_a for chlorobenzene varied by about 10 per cent in different non-polar solvents, being greatest in those with the lowest dielectric constant. Subsequent work has shown that this phenomenon is practically universal, and further that it is highly specific, so that no general relation can be established for correcting the observed moment for the effect of the solvent. The influence depends, as we might expect, for any given solvent on the magnitude of the moment of the solute, and also on the shape of the polar molecules and the position which the dipole occupies in them. Higasi (11) and Frank (6) have tried with some success to examine the relation of these properties, but no complete theory has been reached, or is probably to be expected until the physical theory of liquids has been developed considerably further than it has at present.

This influence of the solvent also affects the accuracy of the determination of the moment by the temperature method in solution, which was previously regarded as exceptionally accurate, since it appears to determine and eliminate the atomic polarization. It is, however, obvious that, since the dielectric constant of the solvent changes with the temperature, the effect on the polarization of the solute will also change. The effect may not be large, but it may seriously change the slope of the polarization-temperature curve, and also the intercept. It will thus give a false value

both of the moment and of the atomic polarization; moreover, owing to the highly specific character of the influence, it is not at present possible to apply a satisfactory correction. In the present state of our knowledge it seems that the accurate determination of the dipole moment is possible only by the measurement of the polarization of the gas over a large temperature range. The next best measurements are those obtained by determining the polarization of the vapor at one temperature, and allowing for the electron polarization through the refractivity.

It is evident that the restriction of accurate measurements to substances whose polarization can be measured in the gaseous state constitutes a very serious limitation of the applicability of the moments, and it is very much to be hoped that it will be possible to discover the general relation between the gaseous and the solution values, so that we may be able to assign moments to molecules that cannot be measured in the gaseous state.

The difficulties of the interpretation of the moments, are not, like those of measurement, obstacles to be got out of the way as soon as possible; they are due to the complications of the molecular structure itself, which is the problem we are trying to solve. They are mainly concerned with two factors,—the mutual polarization of the dipoles and the effects of resonance. One of the chief problems which have so far been attacked by the exact measurement of the moments is that of the valency angles. The resultant of two moments is their vector sum, and so if we know the individual values and the sum we know the angle between them. The difficulty is that the individual moments affect one another by induction; in the chloro derivatives of methane it has been shown (28) that the value may be diminished by as much as 30 per cent. This source of error can only be avoided by having the dipoles whose inclination is to be determined remote from one another. The theory has been discussed by Smallwood and Herzfeld (23) and by Frank (7); for its application in detail to the dichloronaphthalenes see Weissberger and Hampson (34). From this work it is clear that no satisfactory theoretical allowance for the mutual induction can be made unless the dipoles are more than 2 A.U. apart. In practice this means that we are almost confined to compounds of the type



where we can introduce polar groups into the para positions in the benzene rings with the certainty that the new dipoles will be collinear with the X-C valencies. This method has been applied by a number of workers with considerable success to such compounds as diphenylmethane, diphe-

nyl ether, and diphenyl sulfide, and the consistency of the results indicates that it is on the whole trustworthy.¹ The importance of this work lies in the fact that the angle measured is that in which the valencies are attached to two phenyl groups; this may well differ from the angle between the valencies when they are joined to hydrogen or halogen atoms, or to methyl groups, for two reasons: (1) because of the steric interference of the phenyls, which again will vary with the radius of the central atom, and (2) because of the occurrence of resonance forms in which one of the valencies is double. A comparison of the valence angles in these various classes of compounds is thus of great interest. Now it is clear that in the simpler (halogen and alkyl) compounds the dipole method is useless on account of the mutual induction, while the method of electron diffraction is eminently suitable, owing to the relative simplicity of the molecules. In the phenyl derivatives on the other hand the large number of atoms in the molecule makes the calculation of the electron diffraction curves almost impossible, and the angles can only be determined from the dipole moments.

Another subject which has been attacked by the exact measurement of moments is that of the effect of rotating atomic groups, as for example in the ethylene dihalides. This is too complicated a subject to be dealt with here, but reference may be made to the work of L. Meyer (15), Smyth, Dornte, and Wilson (25), Lennard-Jones and Pike (13), and Altar (1).

The second difficulty in relating moment to structure arises from the effect of resonance, and this opens up the widest prospect for the future application of dipole moments.

I need say no more of the theory of resonance than that it implies that certain molecules can have a structure intermediate between two formulas and partaking (but not necessarily in the same degree) of the properties of both. Some of the most convincing proofs of this theory are derived from the study of dipole moment. In no other way is it possible to explain the very small moments of nitrous oxide or of the azide group, where the only permissible structural formulas must have large moments in opposite directions. The simplest example is that of nitrous oxide. Here the spectrum shows that the molecule is linear, but not symmetrical. It must therefore be $\text{N}=\text{N}-\text{O}$, with either two double links, or one single and one triple. Assuming that so stable a substance must have its octets complete, there are two possible structures:



Each of these will have a considerable dipole moment, and in opposite directions, as shown by the arrows. A tautomeric mixture of the two

¹ For a summary of this work see reference 9; for a method of obviating certain difficulties due to resonance see reference 29.

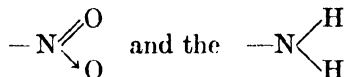
will also be found to have a considerable moment, since the polarization, from which the moment is calculated, is independent of the direction. Now the observed moment of nitrous oxide is only 0.17 *D*; this would only be possible for a tautomeric mixture if the time of interconversion were less than that (ca. 10^{-12} sec.) required for the rotation of the dipoles in the electric field. This practically implies that the molecule is in an intermediate state, which is what we mean by resonance. This conclusion is supported by the dimensions of the nitrous oxide molecule, as deduced from the spectrum (18). Precisely similar arguments apply to the organic azides (21). This is evidently a phenomenon that is peculiarly suited to investigation by means of the dipole moments. It is also one that is of fundamental importance, especially to the organic chemist. The modern theories relating organic reactivity to electron drift, which we owe to Lapworth, Robinson, Ingold, and others, obviously find their physical explanation in the theory of resonance, and should be capable of verification and extension by the dipole methods.

The first example of this is given by Sutton's examination (27) of the difference in moments of the alkyl and aryl compounds $R-X$, in which he showed that the sign of this difference determined whether further substitution occurred in the meta or in the ortho and para positions; this gave an experimental proof of the occurrence of an electronic drift which governed the reactivity.²

More recently, the investigation of resonance by means of dipole measurements has been pursued along a variety of lines. For example, it is known that *p*-nitroaniline has the abnormally high dipole moment of 6.2 *D*, exceeding by about 0.7 *D* the sum of those of aniline (1.52) and nitrobenzene (3.95). This is clearly due to resonance between the forms



and this involves both the



groups in the second formula lying in the plane of the ring. If it were possible to deflect these groups, or either of them, out of that plane, the resonance, and therefore the dipole moment, should be diminished. Now we have evidence that in durene (symmetrical tetramethylbenzene) the

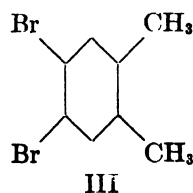
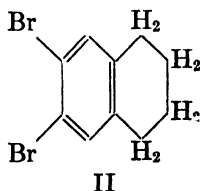
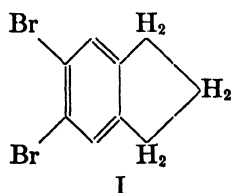
² For attempts toward a theoretical correlation of the resonance with the reactivity see references 32, 14, and 36.

methyl groups should have this effect on an NH_2 or NO_2 placed between them, for in durene itself it has been shown, by x-ray analysis of the crystal (19), that the repulsion of the methyl groups is sufficient to deflect them some 3° from their normal positions. We should therefore expect to find that the moment of *p*-aminonitrodurene is less than that of *p*-nitroaniline, and that a similar reduction of moment occurred with the amino and also with the nitro compounds generally. This question has been investigated by Hampson and Birtles (unpublished work), who found the moments given in table 1 for the durene derivatives as compared with their benzene analogues. It will be seen that in every instance the methyl groups diminish the moment caused by NH_2 or NO_2 , but that with the bromo compound, where no such interference with the resonance can occur, the moments of the durene and the benzene derivatives are identical.

TABLE 1
Moments of certain durene and benzene derivatives

GROUP	DURENE	BENZENE	DIFFERENCE
Nitro-.....	3.38	3.95	-0.57
Amino-.....	1.39	1.55	-0.16
Bromo-.....	1.55	1.52	+0.03
<i>p</i> -Nitroamino-.....	4.98	6.2	-1.2
<i>p</i> -Bromonitro-.....	2.36	2.65	-0.29
<i>p</i> -Bromoamino-.....	2.75	2.99	-0.24

Another question which can be examined by means of the moments is the effect of side rings on the resonance between the Kekulé structures in benzene. Mills and Nixon (16) pointed out that the addition of a side ring of five atoms to benzene, in hydrindene, may, for steric reasons, fix the double links in the benzene ring, with a single link common to the two rings; on the other hand a side ring of six atoms, as in tetralin, might also fix the benzene links, but with a double link common to the two rings. From the reactivities of certain derivatives they obtained evidence in favor of the occurrence of fixation of the links in these ways. It should be possible to test these conclusions by means of the dipole moments of the symmetrical compounds 5,6-dibromohydrindene (I) and 6,7-dibromotetralin (II). If



the links are fixed as Mills and Nixon suggest, the angle between the C-Br valencies should be larger in I than in II, and hence the moments of the systems should differ by an amount which can be calculated within narrow limits and which should be easily detected experimentally. The moments have been measured (22), and compared with those of the corresponding *o*-xylene derivative (III above) and of *o*-dibromobenzene. The results are given in table 2. The moment of the Br—C—C—Br system is obtained by subtracting from the moment of the dibromide that of the parent hydrocarbon together with a small correction (less than 0.2 *D*;

TABLE 2
Dipole moments

TYPE	MOMENT OF HYDROCARBON	MOMENT OF DIBROMIDE	INDUCED MOMENT	MOMENT OF Br—C—C—Br
Hydrindene	0.53	2.48	0.17	1.78
Tetralin.....	0.52	2.81	0.18	2.11
<i>o</i> -Xylene.....	0.59	2.86	0.14	2.13
Benzene.....	0	2.12	0	2.12

TABLE 3
Effect of resonance on moment

COMPOUND	RESONANCE STRUCTURES ← + + →	OBSERVED MOMENT
Carbon monoxide	$\text{C} \equiv \text{O}$ $\text{C} = \text{O}$ $\begin{array}{ccc} \times & \times & \bullet \\ & \circ & \\ \times & \text{N} & \circ \circ \end{array}$ $\begin{array}{ccc} \times & \times & \bullet \\ & \times & \\ \times & \text{N} & \times \circ \circ \end{array}$	0.10 <i>D</i>
Nitric oxide.....	$\text{N} \leftarrow \text{N} = \text{O}$ $\text{N} \equiv \text{N} \rightarrow \text{O}$ $-\text{N} \leftarrow \text{N} \equiv \text{N}$ $-\text{N} = \text{N} \rightarrow \text{N}$	0.16 <i>D</i>
Nitrous oxide.....		0.17 <i>D</i>
Organic azides.....		ca. 0

see references 23, 7, 34) for the moment induced in the side system by the C-Br links.

Thus the dipole moments clearly indicate a fixation of the double links in the sense of the Mills-Nixon theory in the hydrindene system, but not in that of tetralin, where the structure appears to be the same as in the freely resonating systems of benzene and xylene. On the other hand in tetralin the evidence of Mills and Nixon leads to a different conclusion; it indicates that fixation occurs here too, though with a double link common to the two rings. It should be noticed that the evidence from the dipole moments is of a different kind from that derived from the reactivity. In the latter, a relatively small difference in the heat of activation between

two molecules may produce a large change in the rate of reaction, as was pointed out by Sutton and Pauling (32), who concluded that a difference of 6 per cent in the ratio of the coefficients (i.e., in the predominance) of the two Kekulé forms was enough to account for the experimental results of Mills and Nixon. The moments, on the other hand, express the mean position of the atoms in the resting molecule.

In conclusion I may mention one or two points which have arisen from the study of dipole moments, and which still seem to need explanation.

The first concerns the coördinate, semipolar, or dative link. It has been established by a number of examples that this type of link always has a large dipole moment, as its formulation requires. But the moments which are found are much smaller than those required by the simple theory of the transference of an electron. The actual values found vary in different molecules, and often cannot be stated with any exactness, but on the average we take the moment to be about 3 to 4 *D*. Now the average length of the link in these compounds is about 1.5 A.U., so that if the coördination simply involved the transference of an electron from one atom to the other, the moment should be approximately $4.8 \times 1.5 = 7.2$ *D*. The observed difference is presumably due to induction, in which the unshared electrons of the octet no doubt play a large part.

Another point is this. As we have seen, when there are two resonance structures with moments in opposite directions, the result of the resonance is to diminish the moment. The amount of the reduction should be different in every case, depending on the coefficients of the different structures and also on their respective moments, and we have no means of knowing how great it should be. The interesting point is that there is in fact a remarkable tendency for the resulting moment to be very nearly, but not quite, zero. Of this we have at least four examples (see table 3); in the last of them the exact moment of the N₃ group is not known, but that of the whole C—N₃ group is very nearly the same as that of a C—N link, so that the contribution of the N₃ part must be very small.

I should like to express my thanks to Dr. L. E. Sutton and Dr. G. C. Hampson for the kind assistance that they have given me in the writing of this paper.

REFERENCES

- (1) ALTAR: *J. Chem. Physics* **3**, 460 (1935).
- (2) BERGMANN, ENGEL, AND SANDOR: *Ber.* **63**, 2572 (1930).
- (3) DEBYE: *Trans. Faraday Soc.* **30**, 679 (1934).
- (4) ERRERA: *Compt. rend.* **182**, 1623 (1926); *Physik. Z.* **27**, 764 (1926); *Polarisation dielectrique*, Les Presses Universitaires de France, Paris (1928).
- (5) ESTERMANN: *Z. physik. Chem* **1B**, 161 (1928); **2B**, 287 (1928); *Leipziger Vorträge*, p. 17 (1929).

- (6) FRANK: Proc. Roy. Soc. London **152A**, 171 (1935).
- (7) FRANK: Proc. Roy. Soc. London **152A**, 188 (1935).
- (8) FRASER, R. G. S.: Molecular Rays. Cambridge University Press, Cambridge (1931).
- (9) GLASSTONE: Ann. Repts. Chem. Soc. **32**, 126-37 (1935).
- (10) HAMMICK, NEW, SIDGWICK, AND SUTTON: J. Chem. Soc. **1930**, 1876.
- (11) HIGASI: Sci. Papers Inst. Phys. Chem. Research Tokyo **28**, 284 (1936).
- (12) JENKINS, H. O.: Trans. Faraday Soc. **30**, 739 (1934).
- (13) LENNARD-JONES AND PIKE: Trans. Faraday Soc. **30**, 830 (1934).
- (14) MARSDEN AND SUTTON: J. Chem. Soc. **1936**, 599.
- (15) MEYER: Z. physik. Chem. **8B**, 27 (1930).
- (16) MILLS AND NIXON: J. Chem. Soc. **1930**, 2510.
- (17) MÜLLER: Physik. Z. **33**, 731 (1932).
- (18) PAULING: Proc. Natl. Acad. Sci. **18**, 293, 498 (1932).
- (19) ROBERTSON: Proc. Roy. Soc. London **142A**, 659 (1933).
- (20) SIDGWICK: Chem. Rev. **9**, 77 (1931).
- (21) SIDGWICK: Trans. Faraday Soc. **30**, 801 (1934).
- (22) SIDGWICK AND SPRINGALL: J. Chem. Soc. **1936**, 1532.
- (23) SMALLWOOD AND HERZFELD: J. Am. Chem. Soc. **52**, 1919 (1930).
- (24) SMYTH: J. Chem. Physics **1**, 247 (1933).
- (25) SMYTH, DORNT, AND WILSON: J. Am. Chem. Soc. **53**, 4242 (1931).
- (26) SUGDEN: Trans. Faraday Soc. **30**, 734 (1934).
- (27) SUTTON: Proc. Roy. Soc. London **133A**, 668 (1931).
- (28) SUTTON AND BROCKWAY: J. Am. Chem. Soc. **57**, 473 (1935).
- (29) SUTTON AND HAMPSON: Trans. Faraday Soc. **31**, 945 (1935).
- (30) SUTTON AND NEW: J. Chem. Soc. **1932**, 1415.
- (31) SUTTON, NEW, AND BENTLEY: J. Chem. Soc. **1933**, 652.
- (32) SUTTON AND PAULING: Trans. Faraday Soc. **31**, 939 (1935).
- (33) TAYLOR AND SUTTON: J. Chem. Soc. **1931**, 2190; **1933**, 63.
- (34) WEISSBERGER AND HAMPSON: J. Chem. Soc. **1936**, 393.
- (35) WEISSBERGER AND SÄNGEWALD: Z. physik. Chem. **5B**, 237 (1929).
- (36) WHELAND AND PAULING: J. Am. Chem. Soc. **57**, 2086 (1935).
- (37) WILLIAMS: Physik. Z. **29**, 683 (1928).
- (38) WILLIAMS AND FOGELBERG: Physik. Z. **31**, 363 (1930).
- (39) WILLIAMS AND FOGELBERG: J. Am. Chem. Soc. **53**, 2096 (1931).
- (40) WILLIAMS AND WEISSBERGER: J. Am. Chem. Soc. **50**, 2332 (1928); Z. physik. Chem. **3B**, 367 (1929).
- (41) WREDE: Z. Physik **44**, 261 (1927).
- (42) ZAHN: Phys. Rev. **27**, 455 (1926).

THE RELATION BETWEEN THE DIELECTRIC CONSTANTS OF SOME COMPRESSED GASES AND THE DENSITY¹

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INTRODUCTION

The relation of the dielectric constant to density and temperature may be conveniently considered from the point of view of the variation of the Clausius-Mosotti² expression, $\frac{\epsilon - 1}{\epsilon + 2} v$, where ϵ is the dielectric constant, and v the volume of a unit of the substance of interest. The remarkable fact is that gaseous substances may be classified into those for which the C-M expression is practically independent of density and temperature and those for which the function is independent of density but *not* independent of the temperature.

Nearly a quarter of a century has now elapsed since Debye first suggested the basis that accounts for the temperature dependence of the C-M function through the assumption of the existence of permanent electric moments in the molecules of the second classification (polar molecules). During the past eighteen years, moreover, Debye has contributed steadily in expanding the range of application of his original ideas. At the same time an ever increasing number of his fellow scientists have taken part in promoting important advances which have gone far to perfect our knowledge of molecular structure, certain aspects of solution properties, anomalous dispersion and absorption at radio frequencies, and dielectric phenomena generally.

The low pressure gaseous phase is the state most suitable for testing Debye's theory, and the numerous measurements for both gases and dilute solutions of polar substances in non-polar solvents provide ample support for its validity.

In the book *Polar Molecules* (2) care is taken however to emphasize the

¹ Contribution No. 382 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

restrictions surrounding the deduction of the C-M relation in the Debye form which follows:

$$\frac{\epsilon - 1}{\epsilon + 2} v = P = \frac{4\pi N}{3} \left[\frac{a_{11} + a_{22} + a_{33}}{3} + \frac{\mu^2}{3kT} \right] \quad (1)$$

In this equation v is the volume of a mole at the pressure and temperature at which ϵ is measured; P is the molar polarization; N is Avogadro's number; a_{11} , a_{22} , a_{33} are quantities defining the ellipsoid made use of to visualize the dielectric distortion of the molecule; μ is the natural electric moment; and k the Boltzmann constant. Debye states that "In every other case (i.e., other than low pressure gases), for instance in the application of 1 to liquids, the calculation involves certain often questionable assumptions about the interaction with the surrounding molecules. The problem of the calculation of these interactions has, unfortunately scarcely been treated in an adequate manner." The value of high density dielectric constant measurements indeed seems clear as a preparation and foundation for additional theoretical work on the dielectric properties of matter at higher densities. The data most immediately useful are those for the gaseous phase at high temperatures, where the density may be caused to vary with relative ease over a wide range and where quantized collisions are sufficiently infrequent to be of small consequence.

The selection of the material for measurement is also important. Thus considerations relating to molecular coupling are simpler for the gases helium, hydrogen, nitrogen, and methane. These non-polar gases also have relatively low critical temperatures, and measurements made at temperatures from, for example, 50° to 200°C., correspond to temperatures which would be far higher for more complex substances in a comparable state of molecular interaction.³

Moreover, with the exception of methane the gases referred to do not absorb in the infra-red region, a fact which relates to our interest in the L-L refractive index expression. For this very reason however, the case of carbon dioxide is important, since fairly complete data exist for the dispersion of this substance. Finally, data for a polar substance would be welcome, although the problem of theoretical interpretation of a density dependence of the C-M function appears at present somewhat formidable. Ammonia was selected for the measurements, partly because the body of

³ Throughout the remainder of the paper Clausius-Mosotti will be abbreviated to C-M and Lorentz-Lorenz to L-L.

³ The Boyle-point temperature for low pressures may be used as a measure of that state of gas where the effect of the positive and negative molecular potentials balance. On this basis water vapor at 1200°C. would be comparable with nitrogen at about 50°C.

density data is extensive and exact, and partly also because a good deal is known about the structure and physical constants of the molecule. Data will be exhibited showing the variation of the C-M function with density at different temperatures for helium, hydrogen, nitrogen, methane, propane, carbon dioxide, and ammonia. In the case of carbon dioxide sufficient data exist to give an impression of the variation of the C-M expression for the liquid phases over a fairly wide range of density.

THE EXPERIMENTAL DATA

Measurements of the dielectric constants of the compressed gases, air, nitrogen, and hydrogen at 20°C. were made over thirty years ago by Tangl (18) and Occhialini (14, 15) for the purpose of testing the C-M function. Magri about the same time measured the refractive index for air for a range of densities corresponding to a maximum of 200 atm. at 15°C.

He inferred from the data that the L-L expression, $\frac{n^2 - 1}{n^2 + 2} v$, was constant.

Both Tangl and Occhialini first concluded that the C-M function decreased slightly with increasing density (pressures employed up to 334 atm.). This conclusion was later modified and, excluding fluctuations in the measurements amounting to 1 per cent, the C-M expression appeared to be constant.

Other or additional measurements were not reported until after the World War, when data for both compressed gases and liquids appeared. In the meantime the technique of dielectric constant measurement has steadily improved and in addition much of the necessary accurate density data have accumulated for computing the C-M function. Fortunately also for the control and correlation of the higher density dielectric constant data, increasingly exact low pressure measurements have appeared steadily. In brief it seems likely that for several of the gases the C-M function is known over a considerable range to two parts per thousand. It will appear later that the C-M relation should be known to at least this degree of precision if the data are to be of value in guiding theoretical developments.

For helium⁴ and hydrogen⁵ (19) the C-M function shows no definite

⁴ Data obtained at the Massachusetts Institute of Technology and not yet published.

⁵ In the course of preparing the material for the present paper all measurements of dielectric constants which had been made at the Massachusetts Institute of Technology were recomputed. Three different pressure condensers have been used, and corrections peculiar to each were applied for pressure distortion effects. In the case of the measurements reported by Uhlig, Kirkwood, and Keyes, a small error was found to have been made in correcting for distortion. Further perfection in facilities

trend with density or temperature to a density of 6.1 moles per liter (164 cc. per mole) in the case of hydrogen. Recently measurements on hydrogen by Michels, Sanders, and Schipper (13) have been extended to 1425 atm. at 25° and 100°C. without the C-M function showing any definite trend. The case of nitrogen is particularly interesting, because recently Michels, Jaspers, and Sanders (8) have reported values of the C-M expression to a density of 20.6 moles per liter (48 cc. per mole), (1000 atm. at 28° to 150°C.), twice the density reached in our own measurements.⁶ Earlier, Michels and Michels (9) had reported low pressure values. The higher density data appear to show a faint positive trend with density, but the authors (see figure 2 of reference 8) state that "there exists no evidence of a deviation from the C-M relation exceeding the experimental accuracy." Our own values give the impression of a slight density dependence, which perhaps should be stated to be an expectation of a positive rather than a negative trend. Possibly no more definite statement than this can be made in the case of nitrogen, following a careful consideration of all available values of the C-M function.⁷

By way of résumé, the C-M relation for helium and hydrogen, figure 1, shows no systematic variation with either density or temperature. A like statement applies to nitrogen, except that the faint apparent trend of the C-M relation suggests the expectation of a positive rather than a negative density dependence. The average precision of the C-M values is probably not greater than about one five hundredth for these gases. The low pressure L-L function value for the gases⁸ is in very good agreement with the C-M function values at zero pressure.

also made it possible to measure the lead correction of the condenser more accurately. The net effect of the revision of the reduction of the observations is a somewhat smaller Clausius-Mosotti function. A forthcoming publication will give the details of new measurements with the improved, No. 3 condenser.

⁶ The molal volumes for nitrogen were taken in part from recent data by Otto, Michels and Wouters (Physik. Z. **35**, 17 (1934)), and in part from unpublished results by Michels and Gerver.

⁷ Data for air might be considered along with the nitrogen data. Recent measurements have been made by Waibel (Ann. Physik **72**, 161 (1923); 40 atm. at 14°C.), J. W. Broxton (Phys. Rev. **37**, 1338 (1931); also nitrogen), and A. R. Jordan, J. W. Broxton, and F. C. Walz (Phys. Rev. **46**, 66 (1934)). In the third paper the dielectric constant for air is shown to be independent of frequency to 70 kilocycles, and the C-M function shows no large variation. Formerly a minimum in the C-M function was reported at 80 atm. and 18°C. R. McNabney, Wills Moulton, and W. L. Beuschlein (Phys. Rev. **47**, 695 (1935)) also report measurements for air and hydrogen to 335 atm. The C-M function for air shows a maximum deviation of 5 per cent; in the case of hydrogen about 16 per cent.

⁸ Recent precise data for nitrogen have been obtained by Clarence E. Bennett (Phys. Rev. **37**, 263 (1931); **45**, 200 (1934)). L. Ebert and W. H. Keesom found the C-M function for liquid nitrogen the same as for the gas, and Gerald (Ann. Physik **65**, 93 (1921)) found that the L-L function for liquid nitrogen has a value equal to the C-M function.

The case of carbon dioxide is of special interest in view of the type of molecule and the extent and range of data available. It is also very for-

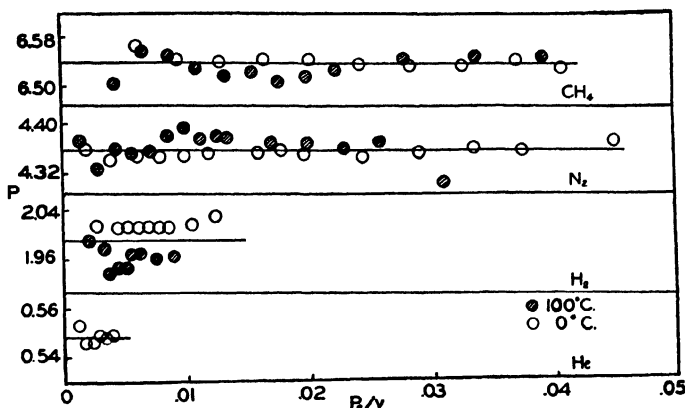


FIG. 1. C-M function for older data obtained at the Massachusetts Institute of Technology

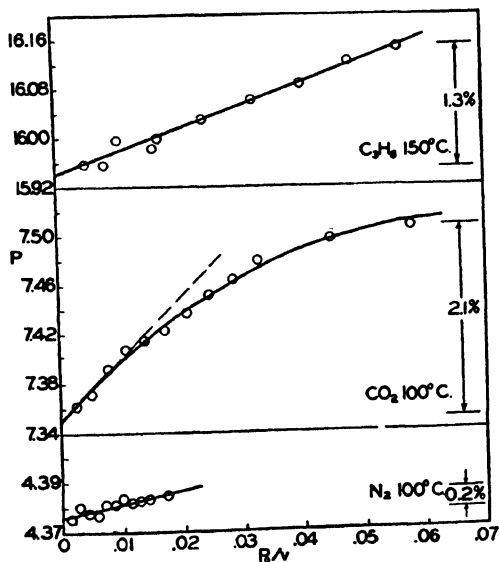


FIG. 2. C-M function; recent data obtained at the Massachusetts Institute of Technology, using the new cell

tunate that new and extensive density data for carbon dioxide are now available (11, 12). Since the data of Keyes and Kirkwood (6), additional

data have been obtained by Uhlig, Kirkwood, and Keyes (19), by Oncley⁹ (shown in figure 2), and by A. Michels and C. Michels (10) for twelve temperatures from 25° to 150°C. and to a density of 25.5 moles per liter (39 cc. per mole, 25°C.; 966.6 atm.). The density data of the 1933 paper were taken from Amagat's work. Later however new data of A. Michels and C. Michels (11, 12) have been used to compute values of the C-M function for the dielectric constant data at 30°, 100°, and 150°C. The 1933 paper of A. Michels and C. Michels, using Amagat's density data, leads to C-M values which the authors state show no effect of temperature but "with increasing pressure the C-M constant shows a tendency to decrease." This statement is apparently opposed to our present conclusion. The data of Michels and Michels at 100° and 150°C. incorporated in figure 3 have, however, been adjusted on the following basis.

It is fairly certain that the molar polarization or the C-M function for carbon dioxide at approaching zero density (P^0) is very close to 7.35 cc. (Zahn, 7.25; Watson, Stewart, McAlpine and Smyth, and Massachusetts Institute of Technology, 7.35 cc.). On examination of the original data of Michels and Michels in the C-M form for the various series of measurements, they exhibit characteristics similar to our own unadjusted data, namely, they do not extrapolate closely to the value 7.35 but instead show a widening spread as lower densities are approached. In fact the Michels and Michels data at 100° and 150°C. may be represented analytically by the following expression

$$P = \frac{a_{-1}}{\rho} + 7.35 + a_1\rho + a_2\rho^2$$

in which the a 's are temperature functions and ρ the density. Now by plotting the expression $\frac{\epsilon - 1}{\epsilon + 2}$ for our original data versus density, it was in general found that the data did not quite lie on a line passing through the zero value of the coordinates. The data of Michels and Michels show a similar effect and when a correction in the amount of the "origin failure"¹⁰ is applied to all the values of $\frac{\epsilon - 1}{\epsilon + 2}$ the systematic trend in the low pressure

⁹ Recent data on nitrogen, carbon dioxide, and propane shown in figure 2 will be published shortly.

¹⁰ The "origin failure" in our cells is due undoubtedly to a variable displacement given the internal parts of the condenser when subjected to stresses induced by the presence of the high pressure gas. Our most recent condenser design (unpublished) was carried out with a view to reducing the amount of the effect, and in practice it has proved almost negligible.

C-M function referred to above is eliminated. The data in figure 3 have been treated in the way described and the inferences relative to trend in

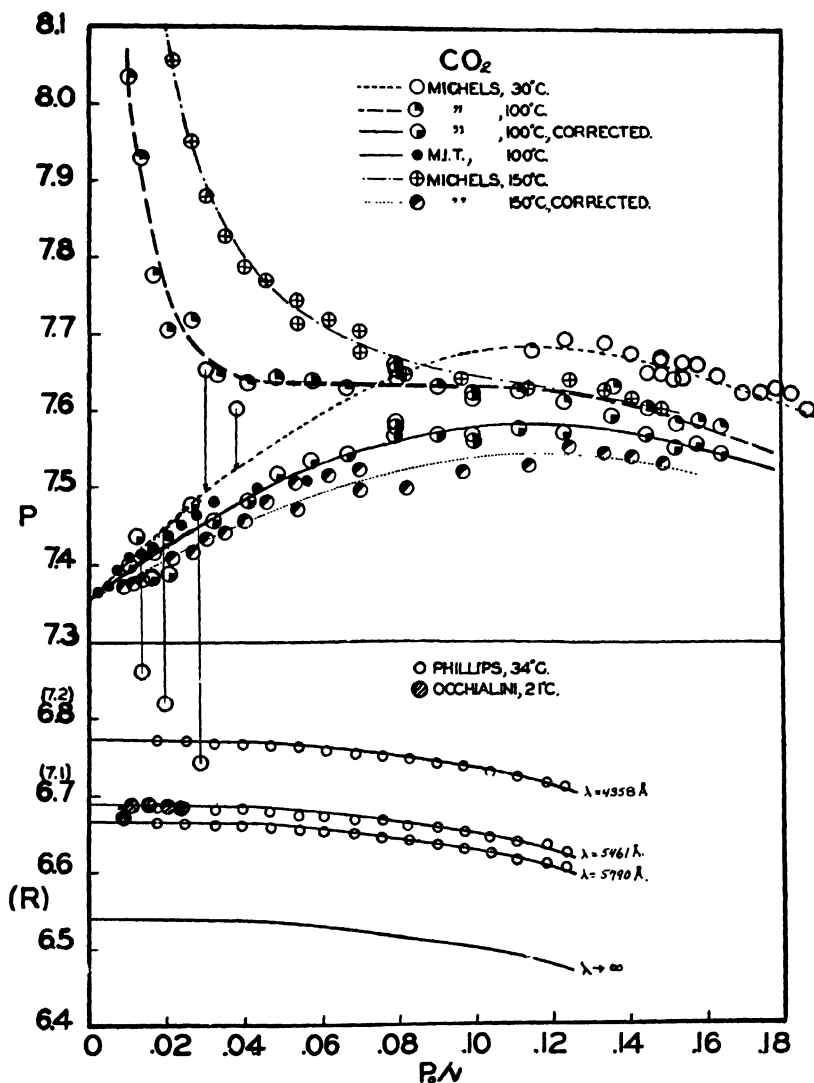


FIG. 3. C-M and L-L functions for carbon dioxide

the C-M function favor a positive trend for the gas or low density phase and a negative trend in the high density phase with a maximum at about 16.3 moles per liter (61.4 cc. per mole; 14 cc. per gram). The inference of

Michels and Michels regarding a negative trend referred to earlier evidently related to the higher densities.

We believe the total available C-M function data for carbon dioxide lead to the following conclusions¹¹:

- (1) The C-M function at higher densities, or at least to a density of 15 moles per liter, exceeds systematically the value 7.35.
- (2) The C-M function exhibits a maximum for P^0/v about 0.12, or 16.3 moles per liter.
- (3) The increase in the C-M function with density at low densities is larger at the lower and smaller at the higher temperatures.
- (4) The C-M values available from all sources are in good agreement.

The refractive index of carbon dioxide has been measured (16; see also 1) over a wide range of wave length values at low pressures and in the visible region over a considerable range of density.¹² Fuchs (3) has formulated all the low-pressure measurements into a single dispersion expression containing four Sellmeier-like terms covering the range $\lambda = 720.4$ A.U. to $\lambda = 14.91\mu$. We may use the formula to compute the L-L expression for $\lambda \rightarrow \infty$ and zero density. The result is 7.28, in very good agreement with the value 7.35, the mean of all the low-pressure values. It is therefore evident that the infra-red absorption characteristics of carbon dioxide account for the low values of the polarization deduced by extrapolation (to infinite wave length) of the data on the index of refraction for visible light.

In the case of propane gas, figure 2, there is also a positive drift of the

¹¹ These conclusions are quite different from those arrived at by P. O. John (Phil. Mag. **22**, 274 (1936)), who discusses the data of Michels and Michels and of Phillips on the basis of the Raman-Krishnan theory (Proc. Roy. Soc. **117 A**, 589 (1928)). He uses the value 7.82 for P^0 ,—a value obtained from a considerable extrapolation of Michels' data to low pressures. All recent determinations show that 7.35 is not far from the correct value.

¹² Phillips found the reciprocal of the L-L function for wave length 5461 A. U. was given by the expression $6.581 + 0.113 \rho^2$, where ρ is the density. Brown reports that the L-L function does not remain constant, and that the $(L-L)^{-1}$ function shows a marked increase at higher densities. The data included densities in excess of 0.8 g. per cubic centimeter. That the $(L-L)^{-1}$ function should be linear in ρ^2 for carbon dioxide seems astonishing, in view of current ideas on the Maxwell relation $n^2 = \epsilon\mu$, where μ is the permeability, leading to the expectation that the sign of the density dependence for the C-M and L-L functions might be similar. It is to be regretted that we lack L-L function data at high densities for structurally simpler substances, for example, the rare gases. As a matter of fact, we do have Magri's findings (Physik. Z. **6**, 629 (1905)) for air densities corresponding to 200 atm. at 15°C., and the L-L function shows no drift. Phillips' values indicate roughly a decline of only 1 in 500 for the L-L function for a 170-fold increase in density,—a rather small density effect.

C-M function with density. At the moment we have no data for the liquid phase.¹³

The only polar gas (figure 4) for which dielectric constant data exist at high densities is ammonia(6). The density data available are very reliable, and the positive trend of the C-M function with density is unmistakable at all temperatures. The permanent moment deduced from the zero density value of the polarization is 1.466 Debye units, to be compared with 1.44 obtained by Zahn and 1.48 by Watson. In fact, there appears

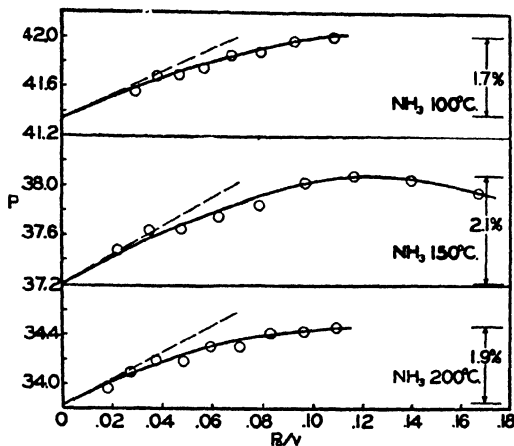


FIG. 4. C-M function for ammonia

to be no change in μ to the highest density¹⁴ (4.48 moles per liter or 223 cc. per mole).

¹³ W. E. Danforth (Phys. Rev. **38**, 1224 (1931)) found that the reciprocal of the C-M function for liquid pentane and carbon disulfide exhibited an inflection in relation to density (corresponding to a maximum pressure of 12,000 atm.). For the latter substance a temperature effect apparently exists (30° and 75°C.) The $(C-M)^{-1}$ function for the polar liquids measured is linear (except for ether) and a temperature function. Charlotte Franks (Ann. Physik **77**, 159 (1925)) also reported dielectric constant values for liquid benzene, heptane, hexane, and carbon tetrachloride to 800 atm. Glenacher in the same volume, p. 138, gives values for a number of polar liquids. There is a negative drift of the C-M relation in every instance with a larger effect for the polar substances. A considerable number of investigators have reported dielectric constant data for liquids under pressure, beginning with Röntgen (Ann. Physik **52**, 591 (1894)). Density data are lacking for computing the C-M function in many cases of interest.

¹⁴ Recently Jeffries Wyman, Jr. (J. Am. Chem. Soc. **58**, 1482 (1936)) has given a summary of the dielectric constant characteristics for a large number of polar liquids. He takes as a basis of correlation the polarization constants of the substances appropriate to the low-pressure gas phase and finds the expression $\frac{\epsilon + 1}{8.5\mu}$ is linear with

CONCLUSIONS

By way of summary of the facts available at this time it appears that in the case of the gases helium, hydrogen, and nitrogen the C-M function is independent of the density and of the temperature. In the case of nitrogen there is possibly a faint indication of a positive trend of the function with density. These gases do not absorb in the infra-red and possess L-L values equal to the C-M values at low densities. In the case of nitrogen there is reason to infer that the L-L function is independent of density, in view of Magri's data on air.

In the case of carbon dioxide, methane, and propane we deal with substances which absorb in the infra-red. The C-M function for the gaseous phase is independent of density and temperature in the case of methane to densities of 6.01 moles per liter (166.3 cc. per mole), and the L-L function is equal to the C-M value. For carbon dioxide below 15 moles per liter, however, the C-M function is not quite independent of temperature and there appears to be a positive dependence on density. The C-M function for the liquid phase of carbon dioxide or for densities exceeding 16 moles per liter appears to show a negative dependence and, considering the gaseous and liquid phase data together, a maximum exists for a density of about 15 moles per liter or a volume of 1.51 cc. per gram. The magnitude of the initial variation of the function is roughly 2 per cent for

reciprocal T . The relation is said to be "fairly satisfactory when applied to the variation of the dielectric constant with temperature and with pressure in the case of a number of polar liquids."

In the succeeding article Lars Onsager (*ibid.* p. 1486) gives a theory for electric moments for molecules in liquids. He shows that the original Mosotti expression for the internal field is not applicable to permanent dipoles. The computational scheme makes use of the excised cavity device in the dielectric (assumed for this portion of the considerations to be a continuum), and a molecular model is employed consisting of a rigid sphere assumed to contain a natural dipole of value μ_0 *in vacuo*. The liquid is envisaged as a close-packed system of the spheres in contact, whose radii are determined from the L-L expression.

One form of the resulting dielectric constant expression is as follows:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\alpha}{a^3} + f(\epsilon, n^2) \frac{4\pi N\mu^2}{9kT}$$

where α is the polarization per spherical molecule of radius a , obtained from the L-L expression, N is the number of molecules in a unit volume of substance, and

$$f(\epsilon, n^2) \text{ is the function } \frac{3\epsilon(n^2 + 2)}{(2\epsilon + n^2)(\epsilon + 2)}$$

The derivative of the function with respect to ϵ is negative and therefore, for constant n , the C-M function would decrease if ϵ increases with pressure. This accords with fact, for as far as known the dielectric constant increases with density without exception, and the C-M function diminishes with increasing density for all polar substances in the liquid phase.

100 atmosphere increase in pressure in the gaseous phase. The C-M function for propane in the gaseous phase is a function of density, but there is insufficient data to indicate a temperature dependence.

The dispersion formula of Fuchs for carbon dioxide at low pressure indicates that the polarization calculated from the L-L function (7.28 cc.) has the same value as that from the C-M function (7.35 cc.). The trend of the L-L function for carbon dioxide with density is, however, opposite in sign to the trend of the C-M function. In fact the reciprocal of the (L-L) function is linear in the square of the density, while the C-M function is almost linear in the density to fairly high densities. If the facts are really as represented, a gap is indicated in our general knowledge of the relation between dielectric and refractive phenomena at higher densities.

The only polar substance for which C-M values exist for the gaseous phase at various densities and temperatures is ammonia. As in the case of the non-polar substances carbon dioxide and propane in the lower density range, the trend of the C-M function is positive and approximately the same for the various temperatures. The value of μ , the polar moment, deduced using the classical Debye theory, appears to be independent of density. The initial density dependence of the C-M function is about 5 per cent per 100 atmospheres.

For liquids the C-M expression trend with density, as far as present evidence goes, is negative and greater for polar liquids than for non-polar. Thus for pentane¹⁵ Danforth found about a 5 per cent decrease in the C-M function for the density increase corresponding to 12,000 atm. and 4 per cent for carbon disulfide, both at 30°C. For chlorobenzene the decrease was at the rate of 19 per cent for 12,000 atm. and 24 per cent for ethyl alcohol, both at 30°C. The magnitude of the decreases does not appear to vary greatly with temperature increase (45°C. interval for chlorobenzene and 30°C. interval for ethyl alcohol). The recent Onsager theory of polar molecules is in general accord with these facts, but a quantitative comparison between theory and fact remains to be completed.

RELATION OF THE FACTS TO THEORY FOR GASES

Various aspects of the unsatisfactory characteristics of Lorentz' (and also Mosotti's, of course) calculation of the local polarization field have been recited by many commentators. The computation is indeed based on an interesting, if not unusual, blend of continuum and discrete-particle argument. The interpretation of the dielectric properties of substances in relation to their molecular structure and other phenomena has, however,

¹⁵ W. E. Danforth observed that the reciprocal of the C-M function was linear in density in the case of polar substances, exclusive of ethyl ether. Carbon disulfide and pentane do not quite follow the rule.

advanced very markedly since the epochal work of Debye, thereby emphasizing the importance of extending and perfecting the theory for the interpretation of the facts. Moreover the recent rapid period of evolution of dynamical theory has led to new concepts of molecular interaction and revitalized old interpretations of physical phenomena, in a way to increase the importance of dielectric phenomena. For this reason there is ground for believing that some of the disabilities of the older theory should be eliminated and progress made in putting the entire theory on a satisfactory statistical mechanical basis. Of course much solid ground must be won before, for example, highly compressed gases or liquids can be dealt with satisfactorily, but even in the latter case Lars Onsager has recently set out some very interesting results.

A modest attempt (7) to form the outline of a molecular statistical theory of the dielectric constant for non-polar molecules may be of interest in connection with the variation of the C-M function with density for non-polar substances. The calculation, of a wholly statistical kind, has led to the following expression

$$\frac{\epsilon - 1}{\epsilon + 2} v = P^0 \left(1 + \lambda \frac{P^0}{v} + \dots \right) \quad (2)$$

where λ is given by the function

$$\frac{P^0}{\beta} \left(1 + \frac{1}{3} \frac{A}{RT\beta} \right)$$

where β and A are constants appropriate to the van der Waals concept of the molecular field.¹⁶ The values of λ derived from the experimental data are given in table 1.

For nitrogen the average magnitude of the density coefficient, $\lambda = 0.1$, would call for less than 1 per cent increase in the C-M function¹⁷ for the highest density measured by Michels, Jaspers, and Sanders, namely, 20.625 moles per liter, corresponding to 1011.6 atm. at 25.3°C. There is reason to believe that $\lambda_{\text{calcd.}}$ for nitrogen should be less than 0.1, owing to an anisotropic fluctuation effect σ .¹⁸ For nitrogen, $\sigma = -0.04$ is obtained

¹⁶ Kirkwood (J. Chem. Physics 4, 592 (1936)) has given a more exact treatment of the problem. He takes account of a neglected item of the earlier paper causing λ to be increased by 5/2. We have used the modified λ in the present comments.

¹⁷ For helium and hydrogen the predicted effect is far less than the experimental error for the highest densities reached in the dielectric constant measurements.

¹⁸ Kirkwood's recent paper (J. Chem. Physics 4, 592 (1936)) on "Anisotropy and Rotational Fluctuations" leads to the following expression for σ :

from Stewart's (17) data assuming the ratio of major to minor axis for the polarization ellipsoid to be in the same ratio as α_1 to α_2 . The value of $\lambda_{\text{calcd.}}$ now becomes almost one-half its early predicted value, or 0.5 per

TABLE 1

Correlation between the density trend of the C-M function and a statistical theory of gaseous dielectrics for non-polar molecules

SUBSTANCE	β IN CC. PER MOLE	$A \times 10^{-6}$ IN CC.-ATM. PER MOLE	P_0	$\lambda_{\text{obsd.}}^{(4)}$	$\lambda_{\text{calcd.}}^{(5)}$
He.....	14.0	0.0216	0.548	*	0.04
H ₂	21.0	0.1975	2.01	*	0.10
N ₂	50.5 (45.9) ⁽¹⁾	1.3445	4.376	*	0.11
CH ₄	55.9 (47.0)	2.2769	6.57	*	0.17
CO ₂	104.8 (47.2)	5.0065	7.35	0.63	0.11 (0.37)
C ₃ H ₈	210.2	13.17	15.94 41.28 ⁽³⁾	0.30	0.12
NH ₃	(40.9)	5.3 ⁽²⁾	37.22 33.86	0.26	2.0 (0.37) ⁽⁵⁾

(1) From viscosity data. All other values are from p - v - T data.

(2) Mean value for 50°, 100°, 150°, and 200°C. For a polar substance A is a strong temperature function at low temperatures.

(3) Values corresponding to 100°, 150°, and 200°C.

(4) Defined from $C-M = P_0(1 + \lambda P_0/v)$. Values are for $\rho \rightarrow 0$.

(5) Value using "distortion" polarization value 6.0.

(6) $\lambda = \frac{P_0}{\beta} \left(1 + \frac{1}{3} \frac{A}{RT\beta} \right)$.

* The precision of the data makes the limiting value of $\lambda_{\text{obsd.}}$ uncertain.

cent and therefore not a great deal larger than corresponds to the present probable experimental error of the C-M values at the highest densities.

In the case of carbon dioxide $\lambda_{\text{obsd.}}$ is about 0.63 for zero density at the average temperatures. The most representative values for β and A for

$$\sigma = \frac{2(\alpha_1 - \alpha_2)}{(\alpha_1 + 2\alpha_2)} \left[\frac{1 - e^2}{e^3} \sinh^{-1} \frac{e}{(1 - e^2)^{1/2}} - \frac{1 - e^2}{e^2} - 1/3 \right]$$

$$= -2/3 \frac{\alpha_1 - \alpha_2}{\alpha_1 + 2\alpha_2} \text{ when } e \rightarrow 1$$

where α_1 and α_2 are the polarizabilities corresponding to the major and minor axes of a symmetrical ellipsoid assumed for the molecular model. The eccentricity for long molecules $e \rightarrow 1$ leads to the second expression.

computing λ is however open to some question.¹⁹ For example, if β is derived from Amagat's data, λ is found to be about 0.11. There is reason to believe, however, that for substances whose critical state is at ordinary temperatures and higher, the value of β derived from viscosity (4) gives a more reliable number. Using then the viscosity data, $\lambda_{\text{calcd.}}$ becomes 0.37. This must be reduced by the amount of the σ whose value is roughly -0.09 , leaving $\lambda_{\text{calcd.}}$ equal to 0.28, or less than one-half the value observed.

It will be further observed that expression 2 requires that λ vary linearly in the reciprocal of temperature. Reference to figure 3 indicates that the slope of the 150°C. low density data is less than for the 100°C. data and this in turn is less than the 30°C. data, in qualitative accord with the requirements of the equation. From equation 2, using the value of β from viscosity data, the initial difference in slopes for the 30°–100°C. data amounts to $\Delta(P_0)_{\text{calcd.}} = 0.31$,—a quantity considerably less than would be deduced from the smooth line for 100°C. and the dotted line for 30°C. It will be noted, however, that the data at lower densities are scarcely precise enough to establish the values of the slopes exactly.

The theory of the dielectric constant for a polar substance along the lines of Keyes and Kirkwood's development has not been carried through. On the other hand, the recent theory of Lars Onsager could scarcely be applied to a gas, as in fact he emphasizes. The value of $\lambda_{\text{obsd.}}$ for ammonia is 0.26, while the value of $\lambda_{\text{calcd.}}$ is 2, an altogether different order of magnitude. If, however, the distortion polarization for ammonia is used in computing λ , the number 0.37 results.²⁰ Of course the value of $\lambda_{\text{calcd.}}$ of the table should be reduced, owing to the Kirkwood anisotropic fluctuation effect σ for a polar molecule. The theory for this effect has likewise not yet been worked out. [We have just learned from J. H. Van Vleck that he has calculated the value of λ for polar molecules. The details will be published elsewhere shortly. In the case of ammonia the computed value of λ is 0.4, in good agreement with our data as regards order of magnitude.]

No reference has been made to "association" as a factor in accounting for departures from the C-M relation. The term does not appear to have any closely defined connotation,—a defect very likely related to the fact that estimates of its magnitude derived from quite varied phenomena seldom lead to comparable numbers. In spite, however, of the often contradictory aspects of applications of the idea, there does exist a well justi-

¹⁹ The values b and a from van der Waals theory using critical data should not be used. See the following section.

²⁰ This fact was noted by H. H. Uhlig in his thesis submitted for the degree of Doctor of Philosophy, Massachusetts Institute of Technology, 1932.

fied impulse to incorporate into certain correlative attempts some allowance for a tendency of molecules to agglomerate or aggregate.²¹

Statistical theory includes within its scope the full possibility of dealing, in principle, with the association or aggregation effect, having its origin in the increasing degree of merging of the molecular fields with density increase. The computational difficulties involved in applications of immediate interest are of course great, and it is for this reason that the application of statistical theory leading to the λ factor was limited to a region where calculations may be made with precision.

The theory of dielectrics attempted by Keyes and Kirkwood, and recently more adequately developed by Kirkwood, is qualitatively in accord with the facts as at present known. Quantitative comparisons will probably, however, never be quite satisfactory using the van der Waals molecular field concept, and a less specialized representation of the field should be employed.

NOTE ON THE QUANTITIES β AND A

The quantities β and A of the λ in equation 2 have the same significance as the b and a of van der Waals theory, except that they are not derived from critical data. Instead they may be derived from actual p - v - T data or from viscosity data. Only in the case of a few of the elementary gases (hydrogen, nitrogen, carbon monoxide) is there a fair accord between β and b , A and a , while in the case of helium and hydrogen at ordinary temperatures and nitrogen above 150°C., the van der Waals molecular field concept is quite inadequate.

It is, however, now well known that the van der Waals equation is quantitatively quite inadequate to represent the p - v - T behavior of fluids, except approximately in certain cases at low pressure. It follows, therefore, that the a and b quantities derived from critical data will in general prove quite valueless for representing accurately the effects of the molecular field appropriate to any given molecule. Values of β and A derived from viscosity data at low pressure or from p - v - T data under favorable conditions may, however, correspond to characteristic values of the molecular field appropriate to the rough approximation of the actual molecular field characteristic of the van der Waals concept.

Some insight into the meaning of the quantities β and A as they relate to the van der Waals concept of the molecular field may be obtained by considering the phase integral for low pressures. The integral may be written as follows:

²¹ One of the authors has on several occasions proposed the term "aggregation" to denote the effect of intramolecular field coupling.

$$B^0 = 2\pi N \int_0^\infty \left(1 - e^{-\frac{\text{Pot.}}{kT}}\right) r^2 dr \quad (3)$$

where B^0 is a pure temperature function in the equation of state, $p = \frac{RT}{v - B^0}$, for low (strictly $p \rightarrow 0$) pressures. The quantity "Pot." represents the molecular potential which may be computed from quantum theory with fair accuracy for helium and hydrogen, for example. The dotted continuous curve in figure 5 represents the course of "Pot." as a function of the distance separating a molecular pair.

The van der Waals concept of the molecular field assumes a spherically symmetrical short range attractive field surrounding the molecules of

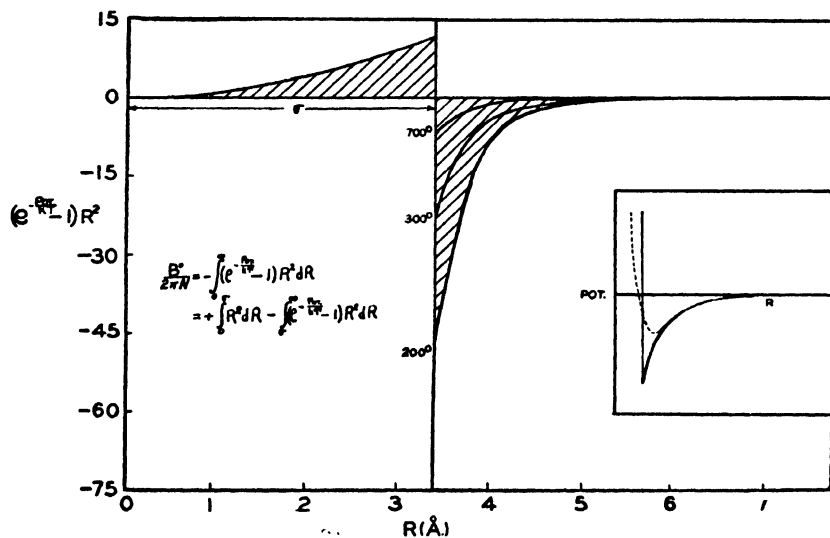


FIG. 5. Potential curve and phase integral

invariable diameter σ . A pair of the molecules in contact are further assumed to develop an infinite repulsion. The trace in a "Pot." vs. R diagram would therefore be represented by the continuous line in the diagram, figure 5, and it is evident that for some molecules the approximation may be too rough for many purposes. In general, where the attractive field or the negative potential is small relative to the repulsion, the approximation will be very bad (case of helium, for example) (5).

The use of the van der Waals concept in evaluating B^0 in equation 3 causes the quantity $e^{-\frac{\text{Pot.}}{kT}}$ to vanish on contact, where "Pot." becomes infinite, and it therefore becomes convenient to consider equation 3 resolved into two integrals as follows:

$$\begin{aligned}
 B^0 &= 2\pi N \int_0^\sigma r^2 dr - 2\pi N \int_\sigma^\infty \left(e^{-\frac{\text{Pot.}}{kT}} - 1 \right) r^2 dr \\
 &= \frac{2}{3} \pi N \sigma^3 - I = \beta - \frac{A}{RT} \sum_{j=1}^{i=\infty} \frac{1}{(2j-1)j!} \left(\frac{A}{RT\beta} \right)^{j-1} \\
 &= \left(\beta - \frac{A}{RT} \right) \text{ for } T \text{ large}
 \end{aligned} \tag{4}$$

when the negative potential varies as the inverse sixth power of the distance.

In figure 5 the graphical scheme for evaluating B^0 of the equation of state is represented for the case of nitrogen, and the discontinuity introduced by the van der Waals concept of an infinite positive potential becomes evident. The approximation will, in general, be more satisfactory at lower temperatures, where the negative area is large relative to the constant positive area, or β .

In practice it is necessary to deduce B^0 (virial coefficient) values from the experimental p - v - T data and relate them to T^{-1} as required by formula 4. If sufficiently high temperature data are available, extrapolation to $T^{-1} = 0$ to obtain β will not be uncertain, as in the case of nitrogen. For carbon dioxide, however, the B^0 data all lie in the negative portion of the B^0 , T^{-1} diagram, and extrapolation to $T^{-1} = 0$ for the "best" value of β becomes difficult.

From the brief statement given it will be clear that representative values of β and A are not easy to obtain for carbon dioxide and for gases of high critical temperature generally. The "constants", particularly β , obtained from viscosity data are in fact likely to be much more reliable for use in representing the effect of the molecular field.

REFERENCES

- (1) BROWN, F. L.: Abstract, Phys. Rev. **43**, 373 (1933).
- (2) DEBYE, P.: Polar Molecules. The Chemical Catalog Co., Inc., New York (1929).
- (3) FUCHS, O.: Z. Physik **46**, 519 (1928).
- (4) KEYES, F. G.: Z. physik. Chem., Cohen Festschrift, p. 709 (1927).
- (5) KEYES, F. G.: Chem. Rev. **6**, 155 (1929).
- (6) KEYES, F. G., AND KIRKWOOD, J. G.: Phys. Rev. **36**, 754, 1570 (1930).
- (7) KEYES, F. G., AND KIRKWOOD, J. G.: Phys. Rev. **37**, 202 (1931).
- (8) MICHELS, A., JASPER, A., AND SANDERS, P.: Physica **1**, 627 (1934).
- (9) MICHELS, A. AND MICHELS, C.: Phil. Mag. **13**, 1192 (1932).
- (10) MICHELS, A. AND MICHELS, C.: Phil. Trans. Roy. Soc. London **231**, 409 (1933).
- (11) MICHELS, A. AND MICHELS, C.: Proc. Roy. Soc. London **153**, 201 (1935).
- (12) MICHELS, A. MICHELS, C., AND WOUTERS, H.: Proc. Roy. Soc. London **153**, 214 (1935).

- (13) MICHELS, A., SANDERS, P., AND SCHIPPER, A.: *Physica* **2**, 753 (1935).
- (14) OCCHIALINI: *Physik. Z.* **6**, 669 (1905).
- (15) OCCHIALINI AND BODAREU: *Ann. Physik* **42**, 67 (1913).
- (16) PHILLIPS, P.: *Proc. Roy. Soc. London* **97A**, 225 (1920).
- (17) STEWART, H. A.: *Molekülstruktur*, table 45, p. 173. J. Springer, Berlin (1934).
- (18) TANGL: *Ann. Physik.* **10**, 748 (1903); **23**, 559 (1907); **26**, 59 (1908).
- (19) UHLIG, H. H., KIRKWOOD, J. G., AND KEYES, F. G.: *J. Chem. Physics* **1**, 155 (1933).

THE DIELECTRIC CONSTANT OF SOLUTIONS OF DIPOLAR IONS

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I. DIPOLAR IONS

In this paper we shall use the term "dipolar ion,"¹ in place of the German expression *zwitterion*, to refer to a particular type of ion usually arising from the dissociation of amphoteric molecules such as the amino acids. A typical dipolar ion is represented by the isoelectric form of glycine, $\text{NH}_3^+\text{CH}_2\text{COO}^-$. Such ions are characterized by the possession of one or more pairs of opposite charges and are electrically neutral. There is now abundant evidence (7), of which that afforded by the study of the dielectric constant of solutions is outstanding, to show that many compounds exist in the form of dipolar ions. Notable among these are amino acids, peptides and proteins, a variety of betaines, and certain phospholipoids.

All the substances so far studied which appear to exist as dipolar ions are wholly insoluble in non-polar liquids;² indeed in general their solubility decreases with decreasing polarity (dielectric constant) of the solvent, an effect no doubt due to the very properties which underlie the formation of dipolar ions. On this account measurements of the dielectric constant of solutions of dipolar ions are restricted to solutions in polar solvents. This would at first seem to deprive the results of much of their value, owing to the lack of any exact theory by which to interpret the dielectric constant of polar liquids. Actually, however, when the subject is approached empirically the situation turns out to be unexpectedly simple, and we encounter certain regular and characteristic effects which not only afford one of the most convincing lines of evidence in favor of the existence of dipolar ions but throw much light on their properties and are moreover of interest in regard to the general problem of the dielectric constant of polar liquids.

¹ This term was first proposed by Ingold (33).

² Dimethylantranilic acid, discussed below in section III, is a possible exception to this.

II. METHODS OF MEASUREMENT

Technically the problem of the measurement of the dielectric constant of the solutions is one of considerable difficulty, owing to conductivity. Water and most of the other solvents for dipolar ions are themselves appreciably conducting, and even with the best preparations available the conductivity of the solution is always greater still. Thus aqueous solutions of the purest preparations of amino acids which have been studied have a specific conductivity in the neighborhood of 50 to 100×10^{-6} mhos at a concentration of 1 mole per liter, or of the order of several hundred times that of ordinary distilled water.

Various methods are available for measuring the dielectric constant of slightly conducting liquids, and most of these have been used by the different investigators who have worked on the problem. The early work of Fürth (27) and Blüh (1) was done with Drude's second method at a wave length of about 76 cm., and more recently Frankenthal (25, 26) and Cavallaro (2, 3) have used the same method. Hedestrand (31) employed an alternating current bridge at a wave length of 300 meters, and Errera (23) also used a bridge in his studies on proteins. Devoto, in his very extensive work on dipolar ions and related molecules, has used throughout Drude's first method at a wave length of about 90 cm. Various forms of resonance method have been used by Walden and Werner (48), Errera (23), and Hausser (30). Shutt (43) has applied Fürth's ellipsoid method to the study of proteins.

There are, however, certain difficulties encountered, either singly or together, in the use of any of these methods in the study of solutions of dipolar ions:—the need of calibration of the circuits with accurately known standard liquids of dielectric constant greater than that of water; the problem of stray capacity effects at the high frequencies made necessary by the conductivity; the requirement of undue amounts of solution at all but very high frequencies (as in Drude's first method); the question of adequately satisfying the ideal conditions of the measurement (as in the ellipsoid method).

In order to avoid these troubles and at the same time to obtain absolute values of the dielectric constant, a new form of resonance method (49) was developed, specifically with a view to study of solutions of dipolar ions, which is adapted for use at high frequencies (3 to 20 meters). The resonant circuit, or resonator, is of fixed shape, designed to possess a suitable inductance and capacity for the frequencies employed, and is made of a single rigid piece of metal with no supporting dielectric material. Such a resonator, which may be gold-plated to give a permanent surface, can be completely immersed in the body of the liquid to be measured by

suspension with a very fine thread which occupies a negligible volume. If this is done, its inductance of course remains unchanged, but its capacity is altered in accordance with the dielectric constant of the liquid. If we denote this by ϵ and refer to the capacity of the resonator *in vacuo* (or, in practice, air) by C_0 , then, since the electrostatic field is wholly included in the liquid, the new capacity is ϵC_0 . Since the resonant frequency of the circuit is given by $1/(2\pi\sqrt{LC})$, L denoting inductance,³ it follows that if f is the frequency of the resonator in the liquid and f_0 its frequency *in vacuo* (or air) the dielectric constant of the liquid is given by $\epsilon = f_0^2/f^2$. In order therefore to measure the dielectric constant of a given liquid, it is only necessary to determine the natural frequency of a suitably chosen resonator, first in air and then in the liquid. Of course air may be replaced by any standard medium of known dielectric constant and the unknown dielectric constant determined in terms of this. It should be noted that the dielectric constant is always given by the ratio of two frequencies; their absolute values do not matter.

In order to determine its natural frequency, the resonator, immersed in the desired medium, is brought into the field of a variable vacuum-tube oscillator, which is coupled with a piezoelectric oscillator of very constant period so as to give beats with it made audible by an amplifier and a pair of telephones. The frequency of the oscillator is then altered by a tuning condenser until resonance is obtained. This is recognized by a sudden change in the plate current of the oscillator, due to an energy exchange between the circuits. The corresponding frequency is then determined by an interpolation based on various nearby beat combinations in terms of the standard frequency of the piezoelectric oscillator.

This method has been used by the author in all of his measurements given below except those on protein solutions discussed in section V.

III. THE DIELECTRIC INCREMENTS OF DIPOLAR IONS AND RELATED SUBSTANCES

A. Amino acids

We will consider first solutions of the monoamino monocarboxylic aliphatic amino acids in water. These ampholytes form a very beautiful homologous series, the members of which differ from one another either in the number of carbon atoms in the chain or in the spacing of the carboxyl

³ This assumes that at the frequency employed the effect of conductivity is negligible. Control experiments at wave lengths of about 5 meters with dilute aqueous solutions of potassium chloride indicate that any systematic errors in the determination of the resonant frequency arising from conductivity lie within the fringe of the experimental errors due to the dullness of the resonance.

and amino groups (as, for example, in the case of an α - and a β -form) or in both these respects. If they exist as dipolar ions there is a positive charge on the amino group and a negative charge on the carboxyl group. The positive charge may be supposed to be located at or close to the center of the nitrogen atom, and, on the basis of resonance, the negative charge midway between the two oxygen atoms of the carboxyl group. As a result of x-ray and electron-diffraction studies there is now fairly exact information as to the internuclear distances of adjacent atoms and the valence angles in the molecules. On the basis of this, assuming that there is no distortion, we may readily calculate⁴ the distance between the positive and negative charges in an α -amino acid to be 2.92 A.U. This distance corresponds to an electric moment of 13.9 A.U. It is not possible to make a similar simple geometrical calculation for other forms in which there are one or more additional carbon atoms between the charged groups, because of the complicating effects of rotation about the valence bonds. The question remains open, therefore, how this distance varies among other members of the series, although it may reasonably be expected to increase with the length of the chain between the amino and carboxyl groups and indeed statistical considerations, discussed below, indicate that it may be, as an approximation, proportional to the square root of the number of intervening atoms. Apart from the amino and carboxyl groups there are no polar groups in the molecules. An outstanding feature of all these amino acids therefore is the extraordinarily large electric moments which they must be supposed to possess as dipolar ions, and which may be expected to find expression in the dielectric properties of their solutions.

The dielectric constant of aqueous solutions of all the amino acids is greater than that of water. The more consistent and apparently reliable results show that there is a linear increase of dielectric constant with the concentration of the amino acid, and a very careful study (52) reveals that this linearity is maintained with a precision equal to that of the best measurements (0.1–0.2 per cent) up to the highest concentrations obtainable—about 2 moles per liter in the case of α -aminobutyric acid, where the dielectric constant is 127, and 2.5 moles per liter in the case of glycine, where the dielectric constant is 135. This simple behavior greatly facilitates the description and comparison of the results, since in any given case these may be expressed in terms of the dielectric increment per mole of solute or the “molar dielectric increment,” a quantity which has in various places been referred to by the symbol δ , but which we denote throughout this paper by $\Delta\epsilon/\Delta c$.

⁴ In this calculation the C–C distance is taken as 1.54 A. U., the C–N distance as 1.4 A. U., the C–O distance as 1.29 A. U., the tetrahedral valence angle as $109^\circ 28'$, and the angle subtended by the two oxygen atoms at the carboxyl carbon atom as 124° . See Stuart (45); also Pauling and Sherman (41).

The values of $\Delta\epsilon/\Delta c$ for all α -amino acids so far studied are not only positive and large, but are all very nearly the same. This may be seen from table 1, in which are summarized results of various workers on a large number of dipolar ions and related substances in water, and to which the reader is referred in connection with all the figures given below. There is a very satisfactory agreement between the results of Devoto at a wave length of 90 cm. ($\Delta\epsilon/\Delta c = 25$ –28), those of Hedestrand obtained with a bridge at 300 meters ($\Delta\epsilon/\Delta c = 23.0$ –23.6) and those of the author at wave lengths between 2.5 and 7 meters ($\Delta\epsilon/\Delta c = 22.6$ –23.2), which shows that there can be no question of anomalous dispersion in this range of frequency. The recent results of Hausser on glycine at 4 meters ($\Delta\epsilon/\Delta c = 30$) are almost certainly too high.

When we consider acids with a greater number of carbon atoms between the amino and carboxyl groups, it is found, just as for the α -amino acids, that the values of $\Delta\epsilon/\Delta c$ are nearly the same for all forms in which this is the same (see table 1) and there is a regular increase of $\Delta\epsilon/\Delta c$ with the number of such intervening atoms. This increase is represented by the following figures, taken from the results of Devoto and of the author as given in table 1, in which n represents the number of intervening carbon atoms (1 for an α -amino, 2 for a β -amino acid, and so on). Because of the small systematic differences the values from the two sources are listed separately, those of Devoto being marked with a single, those of Wyman and McMeekin with a double asterisk.

n	1	2	3	4	5	6
$\Delta\epsilon/\Delta c$	26*, 23**	35*, 33**	51*, 55**	63*	73*, 78**	87*

A scrutiny of these figures shows that $\Delta\epsilon/\Delta c$ increases linearly with n , and indeed by almost exactly 13 for each additional carbon atom. This may be seen in figure 1, in which the averages are plotted.

These facts are at once intelligible if we suppose the amino acids in aqueous solution to exist predominantly as dipolar ions. In the first place the very large values of $\Delta\epsilon/\Delta c$ accord with the enormous moments predicted for such ions, for although it is true that in polar liquids the relation between polarization and dielectric constant cannot be stated quantitatively, there can hardly be any doubt that the two quantities increase together. In the second place the practical identity of $\Delta\epsilon/\Delta c$ for all the amino acids of a given type (α , β , or γ , etc. . . .) suggests a corresponding identity of electric moment such as would be expected whenever the distance between the charged groups is the same, since apart from the effects of these groups there is no other considerable source of polarity in the molecules, and in any case moments of the order of these calculated for dipolar ions would be expected to overshadow everything else. Finally, the regu-

TABLE 1

Values of dielectric increment of dipolar ions and related substances in water

SUBSTANCE	DIELECTRIC INCREMENT
Glycine.....	22.6 (54), * 23.0 (31), 26.4 (8), 30 (30)
α -Alanine.....	23.2 (54), 23.6 (31), 27.7 (8)
α -Aminobutyric acid.....	23.2 (54)
α -Aminovaleric acid.....	22.6 (54)
<i>dl</i> - α -Valine.....	25 (9)
<i>l</i> - α -Leucine.....	25 (9)
β -Alanine.....	34.6 (54), 35 (11), 42.3 (31)
β -Aminobutyric acid.....	32.4 (54), 36 (16)
γ -Aminobutyric acid.....	51 (11)
γ -Aminovaleric acid.....	54.8 (54)
δ -Aminovaleric acid.....	63 (11)
ϵ -Aminocaproic acid.....	77.5 (54), 73 (11)
ζ -Aminoheptylic acid.....	87 (11)
<i>l</i> -Asparagine.....	28.4 (8), 20.4 (29)
<i>l</i> -Glutamine.....	20.8 (29)
<i>d</i> -Glutamic acid.....	26 (9)
<i>l</i> -Aspartic acid.....	27.8 (8)
<i>dl</i> -Proline.....	21 (9)
<i>N</i> -Phenylglycine.....	ca. 30 (17)
Ornithine.....	51 (16)
Sarcosine.....	24.5 (9)
<i>d</i> -Arginine.....	62 (15)
Taurine.....	41 (9)
Creatine.....	32.2 (29)
Glycocyamine.....	30 (29)
Acetylhistidine.....	62 (29)
Glycine dipeptide.....	70.6 (54), 70 (9), 70.5 (2), 80 (30)
Glycine tripeptide.....	113 (54), 128 (2)
Glycine tetrapeptide.....	159 (54)
Glycine pentapeptide.....	215 (54)
Glycine hexapeptide.....	234 (54)
Glycine heptapeptide†.....	290 (52)
Glycylalanine.....	71.8 (29)
Alanylglycine.....	71 (29)
Leucylglycine.....	62 (2), 68.4 (29)
Glycylleucine.....	54 (11), 74.6 (29), 70 (2)
<i>N</i> -Methylleucylglycine.....	67 (29)
Glycylphenylalanine.....	70.4 (29)
Phenylalanylglycine.....	56.7 (29)
<i>d</i> -Leucylglycylglycine.....	120.4 (29), 54 (11), 112 (2)
ϵ , ϵ' -Diguanidodi(α -thio- <i>n</i> -caproic acid).....	151 (29)

* The figures in parentheses give the reference numbers.

† In 5.14 molar urea.

TABLE 1—Continued

SUBSTANCE	DIELECTRIC INCREMENT
ϵ, ϵ' -Diaminodi(α -thio- <i>n</i> -caproic acid).....	131 (28)
Lysylglutamic acid.....	345 (28)
Glycine betaine.....	24-27 (16), 18.2 (22)
α -Aminovalerianic acid betaine.....	60 (30)
ξ -Aminopentadecylic acid betaine.....	220 (70°C.) (30)
π -Aminoheptadecylic acid betaine.....	190 (80°C.) (30)
Pyridine betaine.....	18.5 (22), 20.5 (30)
<i>o</i> -Benzbetaine.....	18.7 (22), 20 (17)
<i>m</i> -Benzbetaine.....	48.4 (22), 58 (17)
<i>p</i> -Benzbetaine.....	72.4 (22), 68 (17), 62 (30)
Thiobetaine.....	23 (16)
<i>N</i> -Dimethylanthranilic acid.....	12 (22), 16.7 (17)
Betaine <i>o</i> -aminophenol.....	5.6 (17)
Betaine <i>m</i> -aminophenol.....	32 (17)
Betaine <i>p</i> -aminophenol.....	45 (17)
Betaine of <i>p</i> -amino- <i>trans</i> -cinnamic acid.....	100 (17)
Betaine of <i>p</i> -sulfanilic acid.....	73 (17)
Betaine of <i>m</i> -sulfanilic acid.....	60 (17)
4,4'-Diphenylbetaine.....	155 (29)
Dimethylphenylglycine.....	17 (17)
<i>o</i> -Aminobenzoic acid.....	Low (13)
<i>m</i> -Aminobenzoic acid.....	41 (13)
<i>p</i> -Aminobenzoic acid.....	ca. 0 (13)
<i>m</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄ CH=CHCOO ⁻	71 (18)
<i>p</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄ CH=CHCOO ⁻ (<i>trans</i>).....	100 (18)
<i>p</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄ CH=CBrcOO ⁻ (<i>trans</i>).....	102 (18)
<i>m</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄ CH=C(C ₆ H ₅)COO ⁻ (<i>cis</i>).....	25 (18)
<i>m</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄ CH=C(C ₆ H ₅)COO ⁻ (<i>trans</i>).....	90 (18)
Phenol.....	-6.6 (8)
Benzoic acid.....	-67 (8)
Aniline.....	-7.6 (8)
Urea†.....	3.4 (8), 3.15 (12), 2.72 (51)
Thiourea.....	4 (8)
Methylurea.....	3.7 (9)
Ethylurea.....	1 (11)
Propylurea.....	1 (11)
Urethan.....	-4.3 (9)
Biuret.....	-6.3 (9)
Semicarbazide.....	0 (9)
Thiosemicarbazide.....	ca. 0 (9)
Dimethylurea (<i>asym.</i>).....	ca. 0 (9)
Dimethylurea (<i>sym.</i>).....	3 (9)
Malonamide.....	4.3 (9)
Succinamide.....	ca. -1 (9)

† The relation is not linear.
increment at zero concentration.

... the limiting value of the

TABLE 1—*Concluded*

SUBSTANCE	DIELECTRIC INCREMENT
Acetamide.....	ca. -0.8 (9)
<i>dl</i> -Malamide.....	2 (16)
Benzamide.....	-4.1 (8)
Sulfamide.....	7 (10)
Nitromethane.....	-2 (16)
Hydantoin.....	-6.4 (11)
Pyrrolidine.....	-1.0 (11)
Pyridine.....	-4.2 (11)
Dimethylpyrone.....	ca. -3 (16)
2,5-Dioxopiperazine.....	-10 (9)
Glycine anhydride.....	-10 (9)
Succinimide.....	-10 (9)
Acetoacetic ether.....	-5.9 (16)
Hydroxylamine.....	-0.8 (16)
β -Indolepropionic acid§.....	-8 (29)
Acetanilide.....	-4 (8)
Acetonitrile.....	-1.74 (8)
<i>m</i> -Dihydroxybenzene.....	-6 (16)
<i>o</i> -Dihydroxybenzene.....	ca. -6 (16)
<i>p</i> -Dihydroxybenzene.....	-6.4 (16)
Methyl acetate.....	-5 (16)
1,2- <i>p</i> -Aminophenylarsenic acid.....	1.2 (16)

§ In 47.05 per cent ethanol.

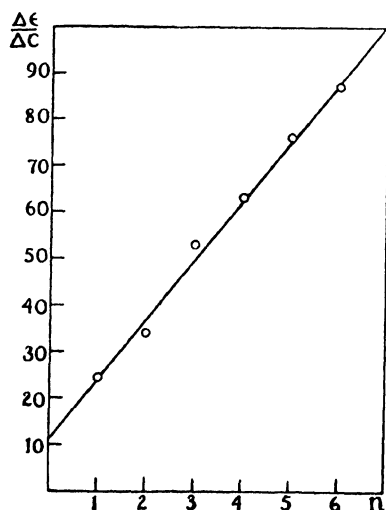


FIG. 1. The dielectric increments of amino acids. n = number of carbon atoms between the amino and carboxyl groups.

lar increase of $\Delta\epsilon/\Delta c$ with the distance between the amino and carboxyl groups indicates a corresponding increase of moment. This would be expected on the basis of a dipolar ionic structure, but hardly otherwise; if the amino and carboxyl groups contribute to the moment simply as ordinary polar configurations there is no reason why the net effect should increase so consistently with their separation in the molecule. The exactly linear form of the increase of $\Delta\epsilon/\Delta c$ with n is more than could have been foreseen simply on the basis of the character of dipolar ions, and has implications which will be taken up later.

This interpretation of the behavior of the amino acids in aqueous solution is confirmed in a very satisfactory way by a study of the moments of their esters, which, unlike the acids themselves, are readily soluble in non-polar liquids. Values of the moments of a number of such esters have been determined by Wyman and McMeekin (55), as given in table 2. Since it

TABLE 2
Electric moments of amino acid esters

SUBSTANCE	MOMENT
	<i>e.s.u.</i> $\times 10^{18}$
Glycine ethyl ester.....	2 11
α -Alanine ethyl ester.....	2.09
α -Aminobutyric acid ethyl ester.....	2.13
α -Aminovaleric acid ethyl ester.....	2 13
Valine ethyl ester.....	2.11
α -Aminocaproic acid ethyl ester.....	2.13
β -Alanine ethyl ester.....	2.14
β -Aminobutyric acid ethyl ester.....	2.11

is well known from a large number of cases that the replacement of a hydrogen atom by a methyl group does not appreciably alter the moment of a molecule,⁵ we may accept the moments of these esters as the same as those of the corresponding amino acids in the unionized state, which cannot themselves be directly measured. If we do this it is apparent from the data in table 2 that unionized amino acids are molecules of very moderate electric moment, not at all such as would be expected to show the very large positive dielectric increments observed in aqueous solution. Various substances not capable of forming dipolar ions but with moments greater than these and soluble in water altogether fail to show such increments. Moreover there is no difference between the moments of the α - and β -forms to

⁵ Thus, for example, the moments (*e.s.u.* $\times 10^{18}$) of acetic acid, methyl acetate, ethyl acetate, and ethyl propionate are, respectively, 1.73, 1.75, 1.81, and 1.79 (see Smyth (44), appendices).

correspond to the pronounced difference in the dielectric increments observed in aqueous solution. Devoto (11) has made a comparison of interest in this connection between γ -aminobutyric acid and its anhydride, pyrrolidone. In the anhydride the formation of dipolar ions is of course impossible, and the value of $\Delta\epsilon/\Delta c$ in water is found to be -1 (11). The moment of pyrrolidone in benzene is given as 2.3×10^{-18} e.s.u. (14), actually somewhat greater than that of amino acid esters.

B. Peptides

The peptides of glycine form a homologous series similar to the aliphatic amino acids, although containing an additional source of polarity due to the amide linkages. Like the amino acids, they may be expected to

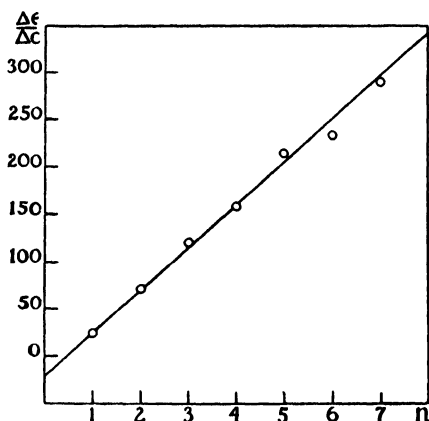


FIG. 2. The dielectric increments of peptides of glycine. n = number of glycine units in the molecule.

exist as dipolar ions, and this is in accordance with the dielectric increments. The first seven peptides of glycine have been studied, the seventh to be sure not in water, where it is very insoluble, but in a 5.14 molar aqueous solution of urea; and the values of $\Delta\epsilon/\Delta c$ are found to increase linearly with the number (n) of glycine units in the peptide, by an amount equal to about 45 for each additional unit, up to a value of 290 for the heptapeptide. This is shown in figure 2. Devoto (9) has found that, in contrast with its isomer glycylglycine, 2,5-dioxypiperazine has a negative molar dielectric increment, -10 .

The study of the dielectric constant in the case of these two series not only affords very strong evidence that the compounds exist as dipolar ions, but suggests a simple correlation between the dielectric increment $\Delta\epsilon/\Delta c$ and the magnitude of the electric moment. This would not of course

enable us to calculate absolute values of the electric moments, but it would make it possible to estimate relative values. That the correlation holds from one series to another, and that $\Delta\epsilon/\Delta c$ does indeed reflect quite directly the magnitude of the moments, is borne out by the fact that the dielectric increment of glycylglycine (70.5) is about midway between that of ϵ -aminocaproic acid (73–77.5) and δ -aminovaleric acid (63), whereas the distance along the chain between the charged groups of the peptide is about the same as in a δ -amino acid. We have taken no account of the contribution to the moment due to the amide linkage. This point of view, which emerges from the study of amino acids and peptides, is greatly strengthened by the results of further studies on solutions of other compounds in water and in other solvents.

C. Betaines

The betaines form a class of compounds closely resembling the amino acids, and in view of their similarity of behavior they, too, must be supposed to exist as dipolar ions (22). For any given amino acid there is a corresponding betaine, which differs from it only in that the three hydrogens of the positively charged amino group are replaced by three organic radicals, represented, in all the cases with which we shall be concerned, by three methyl groups. If in these cases also, as would be expected, the positive charge of the dipolar ion is located at or near the center of the nitrogen atom, the moment of a betaine should be very close to that of the corresponding amino acid, and therefore on the basis of our empirical picture we should expect the dielectric increments of the two to be nearly the same. This turns out to be the case. For glycine $\Delta\epsilon/\Delta c = 23$; for its betaine $\Delta\epsilon/\Delta c = 18$; for δ -aminovaleric acid $\Delta\epsilon/\Delta c = 63$; for its betaine $\Delta\epsilon/\Delta c = 60$. Structurally pyridine betaine ($C_5H_5N^+CH_2COO^-$) and thiobetaine ($((CH_3)_2^+SCH_2COO^-)$ should have moments close to that of glycine betaine (though the S–C distance is 1.8 A.U. as compared with the N–C distance of about 1.4 A.U.) (45, p. 81); actually the corresponding values of $\Delta\epsilon/\Delta c$ are 18.5 and 23. The amino acid with the greatest separation of charged groups so far studied is ζ -aminoheptylic acid. Recently results have been published (30) on the betaines of ξ -aminopentadecylic acid and π -aminoheptadecylic acid, in which there are respectively fourteen and sixteen CH_2 groups between the amino and carboxyl groups (30). The values of $\Delta\epsilon/\Delta c$ are given as 220 at 70°C. and 190 at 80°C. for the ξ - and π -forms, respectively. It was necessary to work at these high temperatures because of the insolubility of the compounds, but it is known that values of $\Delta\epsilon/\Delta c$ do not change rapidly with the temperature. Thus for glycine the dielectric increment changes from 22.58 to only 23.80 between 25° and 0°C. (54). We may therefore consider these values in connection

with other results at room temperature. The fact that the dielectric increment is less for the π - than for the ξ -form is probably due to experimental errors or the presence of impurities. In any case both figures given are in approximate agreement with a continuous increase of $\Delta\epsilon/\Delta c$ by 13 for each additional intervening CH_2 group between the charges, as indicated by data over a more restricted range in the case of the amino acid series. Such an increase would imply values for $\Delta\epsilon/\Delta c$ of 192 and 218 for the ξ - and π -betaines, respectively.

Data are also available for the three benzbetaines (*o*-, *m*-, and *p*-(CH_3) $_3\text{N}^+\text{C}_6\text{H}_4\text{COO}^-$). The values of $\Delta\epsilon/\Delta c$ for the ortho, meta, and para forms obtained by Edsall and Wyman are 19, 48, and 72; the values given by Devoto are 20, 58, and 68. In accordance with our picture, therefore, these betaines also undoubtedly exist as dipolar ions. In these cases the amino and carboxyl groups are attached to the rigid benzene ring. Assuming the ring to be a plane hexagon, 1.39 A.U. on a side, the distances between the charged groups in the undistorted molecules should be 3.23, 5.49, and 6.36 A.U. On this basis the moment of the ortho compound should be slightly greater than that of an α -amino acid; the value of $\Delta\epsilon/\Delta c$ is actually slightly less. In contrast to *o*- and *p*-benzbetaines the *o*- and *p*-aminobenzoic acids have values of $\Delta\epsilon/\Delta c$ close to zero, and this accords with other properties. Thus the aminobenzoic acids have relatively low melting points (140–180°C.), they dissolve appreciably in non-polar solvents, and the dissociation constants of the ortho and para forms imply a ratio of dipolar ions to undissociated molecules in the neighborhood of one (20). Unlike the ortho and para forms *m*-aminobenzoic acid has a dielectric increment of 41, and it is reasonable to assume that in this case the dipolar ions outnumber the unionized molecules. This accords with data on its dissociation constants (20), with the fact that it shows considerable electrostriction (6), and with its heat of reaction with bases (19).

Another molecule closely related to the benzbetaines is *N*-dimethylanthranilic acid ($(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{COOH}$). This shows quite unusual properties (22). Unlike amino acids and betaines it has a low melting point (70°C.), and gives rise to but little electrostriction in water (0.6 cc. as compared with 4.6 cc. for *o*-benzbetaine); moreover, it is very soluble in non-polar solvents. On the other hand its dissociation constants, at least in water and alcohol, indicate that it exists mainly as a dipolar ion, and its dielectric increment is 12, a value less to be sure than that of *o*-benzbetaine, a corresponding dipolar ion, but still indicative of highly polar properties. It is possible, as suggested by Pauling in conversation, that in the case of this molecule the polarity is due not to the structure of a true dipolar ion, but to the formation of a hydrogen bond between the carboxyl and methylated amino groups. This would account for the large moment

measured in benzene, 6.31×10^{-18} e.s.u. Such a value otherwise remains puzzling, for the acid is almost certainly not a dipolar ion in benzene and the moment of its methyl ester, which would ordinarily be expected to be the same as that of the unionized acid, is only 2.05×10^{-18} e.s.u. (22).

This methyl ester of dimethylantranilic acid is also of interest in comparison with its isomers, the benzbetaines. Unlike them it is a liquid under ordinary conditions, having a boiling point of 139°C . at 16 mm. of pressure. Also quite unlike them it is insoluble in water but dissolves freely in non-polar liquids as well as in other organic solvents. In solvents of dielectric constant greater than about 10 it shows negative values of the dielectric increment, and in a mixture of 50 per cent water and ethyl alcohol, where it is still appreciably soluble, $\Delta\epsilon/\Delta c = -9.4$ (22). In the same solvent the benzbetaines all have large positive dielectric increments. From this it is clear that in the case of the betaines, owing perhaps to the bulk of a methyl group as compared with a proton, there is no labile equilibrium between dipolar ions and undissociated molecules governed by the properties of the solvent, such as is indicated for the corresponding amino acids by the study of dissociation constants.

D. Other dipolar ions

Results on various additional substances which have been studied in water are also given in table 1. These include a number of other betaines and related compounds, some of which show very large dielectric increments, as well as several other peptides. It is in accordance with our picture that all the peptides of α -amino acids, whether they contain substituted organic radicals or not, show dielectric increments close to those of the corresponding peptides of glycine. Three peptides, each containing two free amino and two free carboxyl groups, have also been investigated, —lysylglutamic acid, ϵ, ϵ' -diaminodi(α -thio-*n*-caproic acid), and ϵ, ϵ' -diguanyldi(α -thio-*n*-caproic acid). The exceptionally large value of $\Delta\epsilon/\Delta c = 345$ for lysylglutamic acid accords with an extended configuration with a considerable separation of the centers of gravity of the positive and negative charges. The much smaller values of $\Delta\epsilon/\Delta c$ observed for the two other peptides (131 and 151 respectively) imply smaller dipole moments and suggest a considerable amount of rotation about the S-S linkages. The fact that the increment of the diguanido- is greater than that of the diaminopeptide agrees with the fact that the separation of positive and negative charges in both halves of the symmetrical molecule is greater in the former than in the latter.

It may be pointed out here that although many of the cases we have discussed are those of relatively large molecules, there has been no evidence

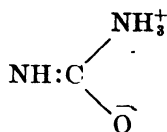
of anomalous dispersion at wave lengths longer than 2.5 meters, such as have been used in the author's measurements, and only for glycylleucine and *d*-leucylglycylglycine do Devoto's results at 90 cm. seem significantly lower than results at longer wave lengths.

The point of view which we have developed enables us to deal empirically with a number of other molecules. Taurine ($\text{NH}_3^+\text{CH}_2\text{CH}_2\text{SO}_3^-$) has a dielectric increment of 41, somewhat greater than that of an aliphatic β -amino acid, and must certainly exist in the ionized form as we have written it. Sarcosine ($\text{N}(\text{CH}_3)\text{H}_2^+\text{CH}_2\text{COO}^-$) behaves like an α -amino acid. The same is true of *dl*-proline, a cyclic amino acid in which the distance between the nitrogen atom and the carboxyl group should be much the same as in an aliphatic α -amino acid. *L*-Aspartic and *d*-glutamic acids both have two carboxyl groups, and in each case the dielectric increment shows that it is the group in the α position with respect to the amino group which is ionized in the dipolar ion. This is in accordance with expectations based on dissociation constants (21). The three diamino acids *l*-asparagine ($\text{NH}_2\text{COCH}_2\text{CHNH}_2\text{COOH}$), *l*-glutamine ($\text{NH}_2\text{CO}(\text{CH}_2)_2\text{CHNH}_2\text{COOH}$), and ornithine ($\text{NH}_2(\text{CH}_2)_3\text{CHNH}_2\text{COOH}$) have dielectric increments of 20 or 28, 21, and 51, respectively. In the two former compounds therefore it is the α -amino group, in the latter compound the more distant amino group which dissociates. This shows the effect of an amide linkage on the properties of the NH_2 group. The dielectric increments of creatine ($\text{NH}:\text{C}(\text{NH}_2)\text{NCH}_2\text{CH}_2\text{COOH}$) and glycocyamine ($\text{NH}:\text{C}(\text{NH}_2)\text{NHCH}_2\text{COOH}$), 32 and 30, respectively, are close to those of β -amino acids, although somewhat less, and the compounds must both be supposed to exist predominantly as dipolar ions. In these cases, owing to resonance, the positive charge should probably be regarded as located on the terminal carbon atom bearing the two nitrogens. *d*-Arginine ($\text{NH}:\text{C}(\text{NH}_2)\text{NH}(\text{CH}_2)_3\text{CHNH}_2\text{COOH}$) has a dielectric increment of 62, and here again, owing to resonance, it is probably the terminal carbon atom between the nitrogens which carries the positive charge. In acetylhistidine, also with an increment of 62, one of the nitrogens in the ring must bear a charge.

E. Amides

Carbamide and various substituted ureas which have been studied form an exceptional group of compounds. For the most part their aqueous solutions have dielectric constants greater than that of water, but the relation between dielectric constant and concentration, at least for carbamide itself, is not linear; and the values given for the dielectric increments, however estimated, are all much less than for amino acids, the greatest being 7 in the case of sulfamide, $\text{SO}_2(\text{NH}_2)_2$. In view of their positive

dielectric increments it has been suggested that they exist as true dipolar ions, for example,



in solution (9). They do not however, so far as data are available, show the electrostriction characteristic of dipolar ions. It is probably more correct to interpret the behavior on the basis of a resonance effect, whereby the carbon atom may be regarded as bearing a negative, and either one of the nitrogens a positive, charge (42). This is in accordance with the rela-

TABLE 3
Electric moments of various amides

SUBSTANCE	MOMENT	REFERENCE
	c.s.u. $\times 10^{18}$	
Dimethylurea, symmetrical.....	4.8	(32)
Tetraethylurea.....	5.1	(14)
Propylurea.....	3.3	(14)
Acetamide.....	4.1	(14)
Sulfamide.....	3.6	(14)
Benzamide.....	3.9	(14)
Valeramide.....	3.6	(14)
Caproamide.....	3.7*	
	3.9*	

* From unpublished measurements of Wyman on benzene solutions. Polarizations decrease rapidly with concentration.

tively large moments of a number of these amides in non-polar solvents, given in table 3.

F. Dielectric increments in solvents other than water

A consideration of the dissociation constants of the amino acids and their esters in aqueous solution indicates an overwhelming preponderance of dipolar ions over undissociated molecules. Corresponding considerations in the case of solutions in alcohol-water mixtures indicate a steady diminution in the proportion of dipolar ions with an increase in the percentage of alcohol; nevertheless even in 90 per cent alcohol the ratio of dipolar ions to uncharged molecules should be of the order of 500 or 1000 to one (21). It is in accordance with this that the dielectric increments of amino acids in alcohol-water mixtures are all characteristically large. Beyond this

point of general agreement, however, there emerges the unexpectedly simple result that the numerical value of the dielectric increment of a given amino acid remains almost unchanged with varying composition of the alcohol-water solvent (52). This fact, without regard to any theoretical implications it may have, is further evidence for our purely empirical conception of the dielectric increment as a very direct, simple, and significant expression of the polar properties of the dissolved molecules. At the same time it at once raises the question how far this constancy of the values of the dielectric increments persists in other solvents, where the molecules may be expected to exist primarily in the form of dipolar ions and therefore possess the same characteristic moments.

Data in regard to this question are provided by studies (52) on the dielectric increments of two amino acids, glycine and α -aminobutyric acid, dissolved in aqueous solutions of urea and of each other. Although the

TABLE 4
Solutions of α -aminobutyric acid (25°C.)

SOLVENT	ϵ^*	$\Delta\epsilon/\Delta c$
80 per cent ethyl alcohol.....	35.37	24.0
60 per cent ethyl alcohol.....	47.20	22.1
40 per cent ethyl alcohol.....	59.41	22.6
20 per cent ethyl alcohol.....	69.82	23.6
Water	78.54	23.5
2.58 molar urea.....	87.37	20.9
0.961 molar glycine.....	99.8	23.1
1.993 molar glycine.....	124.05	19.0
2.510 molar glycine.....	134.9	18.4

* The dielectric constant of the solvent.

dissociation constants have not been determined under these conditions, the dielectric constants of the solutions are in all cases high, and it is reasonably certain that the amino acids exist overwhelmingly as dipolar ions. The results on α -aminobutyric acid, together with the results on solutions in alcohol-water mixtures, are given in table 4. The results on glycine are essentially the same. It is apparent that the dielectric increment remains remarkably constant in all these solvents.

Similar data are available for the three benzbetaines and glycine betaine, which, as we have pointed out, probably exist wholly in the form of dipolar ions under all conditions. In figure 3 are shown the results of Edsall and Wyman (22) on solutions in ethanol-water and ethanol-benzene mixtures, and in figure 4 hitherto unpublished results of the author on solutions in

dioxane-water mixtures.⁶ It is apparent that in solvents of dielectric constant greater than 20 or 25 the values of the dielectric increment remain

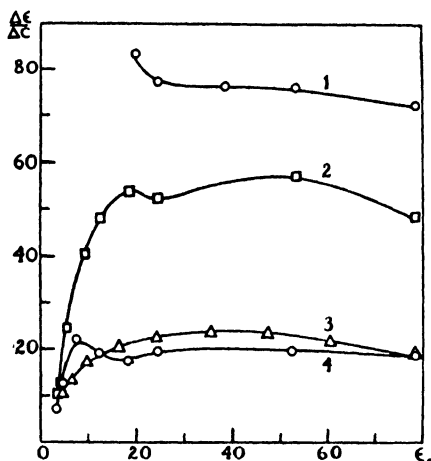


FIG. 3. The dielectric increments of betaines dissolved in ethanol-water and ethanol-benzene mixtures. ϵ_0 = dielectric constant of solvent. 1 = *p*-benzbetaine; 2 = *m*-benzbetaine; 3 = *o*-benzbetaine; 4 = glycine betaine.

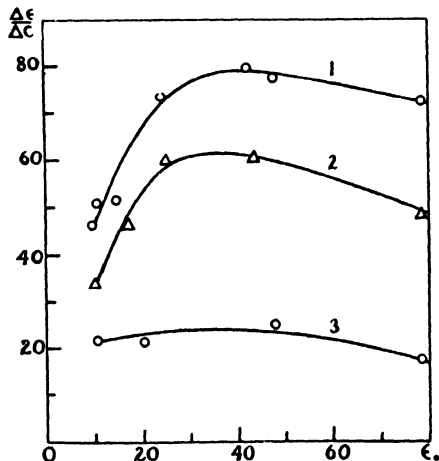


FIG. 4. The dielectric increments of betaines dissolved in dioxane-water mixtures. ϵ_0 = dielectric constant of solvent. 1 = *p*-benzbetaine; 2 = *m*-benzbetaine; 3 = *o*-benzbetaine.

⁶ In certain cases, always in solvents of dielectric constant less than 25, the dielectric constant-concentration relation, $d\epsilon/dc$, is not linear, diminishing with the concentration. In these cases the values of the dielectric increment plotted in the figure are the estimated values corresponding to zero concentration.

fairly constant and there is no considerable difference between the two sets of solvents. This is like the case of the two amino acids studied. In solvents of dielectric constant less than 20 or 25, the dielectric increments decrease markedly with the dielectric constant of the solvent, specific differences between the solvents become larger, and in general the situation is complicated. We shall not attempt to discuss it here.

All that we wish to emphasize at this point is the way in which the facts fit into an essentially simple picture, which emerges from a consideration of all the data on solutions of dipolar ions in solvents of high dielectric constant, and of which the main features are the following: linear variation of dielectric constant with the composition of the solution; characteristically large values of the dielectric increments; close correlation of these with the relative magnitudes of the electric moments; their approximate independence of the nature and dielectric constant of the solvent. From this picture it appears that to a certain unexpected extent, in the case of strongly polar liquid systems, the dielectric constant is an additive property.

III. THE INTERPRETATION OF THE DIELECTRIC CONSTANT OF POLAR LIQUIDS

In the previous section we have made no attempt to account for the character of the results in terms of the theory of the dielectric constant or to estimate numerical values of polarizations or moments. We have simply made use of the general point of view that the magnitude of the dielectric constant is positively correlated with the polarization. In this section we shall deal tentatively with both these matters.

It is clear at the start that the additive character of the dielectric constant, which is such an essential feature of the results, can hardly be accounted for on the basis of Debye's theory, developed primarily to deal with gases and dilute solutions in non-polar solvents. For in any system it is the polarization which is fundamentally the additive property, and in accordance with this theory the relation between dielectric constant and polarization per unit volume (p) is not linear but corresponds to a hyperbola:

$$p = \frac{\epsilon - 1}{\epsilon + 2} \quad (1)$$

In the case of a dipolar ion like α -aminobutyric acid, where the dielectric constant is so exactly linear in the concentration and the molar dielectric increment varies so little between different solvents, we should have to invoke an almost incredible degree of compensating variation in the polarizations to account for the facts in accordance with equation 1, for, owing to the nature of the function, ϵ is exceedingly sensitive to p in all media of high dielectric constant:

$$\frac{pd\epsilon}{\epsilon dp} = \frac{(\epsilon + 1)(\epsilon - 1)}{3\epsilon} \quad (2)$$

For example, if we assume the polarization of the solvent to be independent of the concentration of solute, this would be represented by a very exactly prescribed decrease in the polarization of the dipolar ions, on the one hand with increasing concentration in a given solvent and on the other hand with increasing dielectric constant of the solvent at a given concentration.

It is equally clear that the Debye theory fails to give satisfactory results when used to calculate the moments of the dipolar ions. Thus, taking account of optical polarizations, we arrive at the following moments (E.S.U. $\times 10^{18}$), based on data in water at a concentration of 0.2 mole per liter: glycine, 1.30; α -alanine, 1.51; α -aminobutyric acid, 1.67; α -aminovaleric acid, 1.79; β -alanine, 1.58; β -aminobutyric acid, 1.73. These results are unreasonably small, in all cases actually less than the moments of the esters of amino acids measured in benzene, which are close to 2.12×10^{-18} E.S.U. Moreover, the regularity which is so apparent in the values of the molar dielectric increment is completely lost; and the values for the moments of the larger α -amino acids are actually greater than those of the smaller β -amino forms.

This is only a particular instance of a general difficulty always encountered in the application of the theory to media of high dielectric constant. Owing to the nature of the equation (1), it follows that as the dielectric constant increases, the polarization per unit volume increases more and more slowly and approaches unity as a limit when ϵ tends to infinity.⁷ It is for this reason that in highly polar media calculated values of polarizations per mole are limited by the partial molal volumes, which they approach whenever the dielectric constant is large; and this effect masks everything else. Indeed, even in the case of dilute solutions in non-polar solvents there is now evidence, owing to the very careful work of Müller (39), that this same difficulty is appreciable.

Various attempts have been made to deal with this effect in calculating the values of moments from data on solutions. For instance, van Arkel and Snoek (46) have attempted to do so by modifying the expression for the dipole portion of the polarization in terms of the electric moment. The phenomena exhibited by solutions of dipolar ions in polar liquids forcibly suggest quite another and more radical point of view. It appears that the only simple way to account for a body of facts which would otherwise constitute a set of very unlikely coincidences is to assume that in media of high dielectric constant the relation between dielectric constant and polarization is linear:

⁷ This corresponds to the Curie point.

$$\epsilon = a + bp \quad (3)$$

where p denotes polarization per unit volume, a and b are constants, and $a < \epsilon$. If we accept this point of view it follows at once that whenever the volume polarization of a solution varies linearly with its composition the dielectric constant must do likewise. At the same time we have a ready explanation of the approximate constancy of the dielectric increment from solvent to solvent, and of its sameness for dipolar ions having moments of about the same size. If we assume the polarizations and partial molal volumes of solute and solvent to be independent of concentration, and if we denote by V the partial molal volume of the solute, by C its concentration in moles per liter, by P its molar polarization, and by ϵ the dielectric constant of the solvent, it follows from equation 3 that

$$\frac{d\epsilon}{dc} = \frac{bP - V(\epsilon_0 - a)}{1000} \quad (4)$$

The data show that the effect of the second term on the right is small for dipolar ions; thus in water the ratio

$$V\epsilon_0/(1000 \, d\epsilon/dc)$$

is but 0.15 for glycine and 0.07 for the heptapeptide of glycine. From this it follows that the dielectric increment should be approximately proportional to the molar polarization, or, since the optical polarization is a negligible fraction of the total, to the square of the electric moment. This way of accounting for the situation was suggested by the writer, in a somewhat more specific form (52), and it has been adopted by Werner Kuhn (36). Recently it has been discussed further (53).

From a physical point of view the interesting implication of a linear relation between dielectric constant and polarization is in regard to the internal field. In accordance with the classical theory it follows that the ratio of this to the electric intensity increases without limit as the volume polarization approaches unity. On the basis of a linear relation it follows at once from the fundamental equations that the ratio remains finite when p increases indefinitely (53). This would be accounted for by the interaction of the molecules in the interior of the liquid, as Onsager (40) has attempted to do.

From a chemical point of view a linear relation has interesting implications with regard to the configuration of the dipolar ions in solution, although of course it is impossible to estimate numerical values of the moments without a knowledge of the constants. We have seen from the study of aliphatic amino acids and betaines and of peptides that the dielectric increment increases linearly with the length of the chain between the

oppositely charged groups in the molecule. Since it follows from equation 4 that the dielectric increment is approximately proportional to the square of the moment, this implies that in these cases the average value of the square of the distance between the charged groups also increases linearly with this length. This agrees with statistical deductions. Eyring (24) and Werner Kuhn (35) have both derived expressions for \bar{C}^2 , the mean square distance between the ends of a "straight"-chain structure in which there is free rotation about valence bonds but no distortion of valence angles, and agree that as an approximation this quantity should be proportional to n , the number of atoms in the chain.⁸ In these derivations no account is taken of the volume occupied by the chain or of the effects of forces between various parts of the molecule. In the case of dipolar ions the electrostatic attraction between the oppositely charged groups at the ends of the chain would be expected to reduce \bar{C}^2 considerably. In a more recent discussion Kuhn (36) has shown that this is so even in water where the dielectric constant is high, although the approximate proportionality of \bar{C}^2 and n is not affected. By taking account of this attraction and assuming a value of 1.5 A.U. for the distance of closest approach of the charged groups in amino acids, Kuhn calculates the following mean square values of the distance between the charges in relation to Z , where Z is 2 more than the number of CH_2 groups separating the amino and carboxyl groups:

Z	3	4	5	7	9	12	16	25
$\bar{C}^2(\text{A.U.}^2)$. . .	3.88	5.54	7.3	11.6	16.4	24.5	38.2	69

Kuhn also develops an argument to show that any distortion of dipolar ions (e.g., stretching) due to the application of an external field makes no difference to their polarizations, so that the effective moments should be the same as those due to mean square distances as they exist in the absence of an external field.

These considerations lend support to the view that in strongly polar liquids the relation between dielectric constant and volume polarization is linear. Quite recently an attempt has been made to obtain other evidence in regard to this point from a consideration of pure liquids (53). One hundred and forty cases were considered in which there are data on the dielectric constant as well as on the electric moments. As a tentative pro-

⁸ Eyring's formula is

$$\bar{C}^2 = C_1^2 [n + 2(n-1) \cos \theta + 2(n-2) \cos^2 \theta + \cdots + 2 \cos^{n-1} \theta]$$

where θ is the supplement of the valence angle, C_1 is the distance between the centers of adjacent atoms of the chain, and the length of the chain is nC_1 . Kuhn's formula is

$$\bar{C}^2 = nC_1^2 \left(\frac{1 + \cos \theta}{1 - \cos \theta} \right)$$

cedure hypothetical values of the volume polarizations of the liquids were calculated by assuming for the liquid state the same molar polarizations as are found in the vapor or in solutions in non-polar solvents, and by taking account of the number of molecules per cubic centimeter. These hypothetical values of the volume polarization were then compared with the dielectric constant. Except in the case of relatively few liquids such as formic acid, prussic acid, water, formamide, and various alcohols, which are generally supposed to be strongly associated, owing to the formation of hydrogen bonds, and are anomalous in many respects (for example, see Kumler (37)), the results indicate a linear increase of dielectric constant with polarization which is fairly satisfactory in view of the nature of the procedure. A similar treatment of data on individual liquids over a range of temperature and pressure also gives results in accordance with a linear relation between polarization and dielectric constant.

We may try the effect of using these data to estimate rough values of the constants in equation 2. b then turns out to be between 6 and 10 and the best value appears to be close to 8.5; a is small, about equal to -1 . Moments ($\times 10^{18}$ E.S.U.) of several dipolar ions calculated from equation 4 on the basis of $b = 8.5$ and $a = -1$ are as follows: glycine, 12.2; β -alanine, 15; γ -aminobutyric acid, 18; δ -aminovaleric acid, 20; ϵ -aminocaproic acid, 22; glycine tetrapeptide, 31; glycine hexapeptide, 38. The corresponding moments calculated from the values of \bar{C}^2 given by Kuhn are 9.4, 11, 13, 15, 16, 24, and 32, respectively. For the longer chain molecules the agreement is moderate. Kuhn's values for the smaller molecules, such as glycine and β -alanine, are almost certainly too small, since the value of 1.5 A.U. assumed for the distance of closest approach of the amino and carboxyl groups is too small, and since in any case the treatment is not applicable to α -amino acids, where free rotation does not affect the moment, and is probably not well suited to the shorter chain molecules generally. As we have seen, on the basis of atomic dimensions we should predict a moment for glycine of 13.9×10^{-18} E.S.U., and recent calculations based on the application to solubility data of a model developed by Kirkwood (34) give a moment of 15.2×10^{-18} E.S.U.

Onsager (40) has very recently developed a treatment of the dielectric constant of liquids which would appear to account for all this in a most satisfactory way, indeed even to the numerical factors. According to his theory the value of b is determined by the "internal refractive index" of the molecules. If this is taken as 1.46, b turns out to be 8.5, the value obtained empirically from the data on the liquids. a is negligible in comparison with ϵ .

IV. ANOMALOUS DISPERSION OF DIPOLAR IONS

Among the ampholytes existing as dipolar ions the proteins may be expected to show exceptional dielectric properties, owing to their enormous size and the great number of dissociating groups possessed by even the most inert of them. The recent work of Svedberg and others shows that the molecular weights range from a value of 1700 to 3000 for clupein (38), the smallest protein molecule so far studied, up to values of several million in the case of certain hemocyanins. For molecules of this size we may expect large relaxation times and anomalous dispersion at radio frequencies.

The number of free dissociable groups in a protein is determined by the number of diacidic and dibasic amino acids which it contains, and if there is no ring formation it is two more than this number. The moment of the protein molecule as a dipolar ion is determined by the number of pairs of positive and negative charges which it carries as a result of the ionization of such groups and by their relative positions in the molecule. In all proteins this number appears to be considerable. For example, even in such an inert protein as zein it is about 6⁹ and in egg albumin it is 27 (5, 47). Although little or nothing is known as to the spacial arrangement of these groups in the molecules, it is evident that in general the proteins may be expected to have unprecedentedly large resultant moments even among dipolar ions.

Fürth (27) early studied aqueous solutions of two proteins, "Kahlbaum's albumin" and gelatin, by means of Drude's second method at a wave length of 90 cm., and found that the dielectric constant of the solutions was less than that of water. The negative dielectric increments obtained by Fürth are in no way inconsistent with the character of the proteins as dipolar ions of large moment, for, as we have seen, it would be expected that at 90 cm. he was working within or below the region of anomalous dispersion. That this is the case has since been clearly shown by measurements of the author (50) on solutions of the plant protein zein in 70 per cent *n*-propyl alcohol over a range of temperatures and wave lengths, and by more recent work of Errera (23), Calvallaro (3), and Shutt (43). The results of all these investigators show that at longer wave lengths the proteins have large positive dielectric increments. Thus in the case of egg albumin dissolved in water Shutt's results (at 200 cycles per second) indicate a value of the dielectric increment of approximately 4000, and Errera's results (at wave lengths up to 20,000 meters) a value of about 10,000. In spite of the quantitative discrepancy it is evident from this that egg albumin must have an enormous moment: values calculated from these figures by means of equa-

⁹ See Cohn, Berggren, and Hendry (4). The value 16, given in their paper, is based on a molecular weight now known to be about three times too large.

tion 4 are of the order of 200×10^{-18} e.s.u. Other proteins appear to have similarly large dielectric increments.

It is of interest to consider these results quantitatively in terms of Debye's theory of anomalous dispersion. In accordance with this the measured value of the dielectric constant drops from an upper static value ϵ_0 to a lower limiting value ϵ_∞ as the frequency of the measurement is increased to such a point that the dipoles can no longer follow the alternating field, in accordance with the following equation,

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + x^2 \nu^2} \quad (5)$$

where

$$x = 2\pi\tau \frac{(\epsilon_0 + 2)}{(\epsilon_\infty + 2)}$$

and τ denotes the relaxation time and ν the frequency. The frequency ν_c at which the dielectric constant is midway between the upper and lower values, i.e., $\epsilon = (\epsilon_0 + \epsilon_\infty)/2$, is given by

$$\nu_c = \frac{1}{2\pi\tau} \frac{(\epsilon_\infty + 2)}{(\epsilon_0 + 2)}$$

If we are dealing with a solution there should be a region of anomalous dispersion for each component determined in accordance with equation 5 by the relaxation time of each. If instead of the classical relation between dielectric constant and polarization we assume any linear relation such as that apparently prevailing in highly polar media, it is easy to show that the expression for x is replaced by $x = 1/2\pi\tau$ and $\nu_c = 1/2\pi\tau$. The form of the dispersion curve is therefore the same whether one assumes the classical or the linear relation, and if ϵ_0 and ϵ_∞ are both large, as in the case of a protein in aqueous solution, the numerical value of ν_c is approximately the same on the basis of either interpretation of the dielectric constant.

The results on zein may be fitted satisfactorily by equation 5. This is shown in figure 5, in which is plotted the dielectric constant of a 4.2 per cent solution against the logarithm of the frequency at two temperatures. The smooth curves are calculated from equation 5 with the following choice of constants: at 69.5°C., $\epsilon_0 = 40.5$, $\epsilon_\infty = 27.0$, $x = 2.58 \times 10^{-7}$; at 50°C. $\epsilon_0 = 41.0$, $\epsilon_\infty = 29.8$, $x = 3.91 \times 10^{-7}$. On the basis of the classical theory these values of x correspond to relaxation times of 2.8×10^{-8} sec. and 4.6×10^{-8} sec. at 69.5° and 50°C., respectively; on the basis of a linear relation the corresponding values are 4.1×10^{-8} sec. and 6.2×10^{-8} sec. The measured viscosities at the two temperatures, to which of course the relaxa-

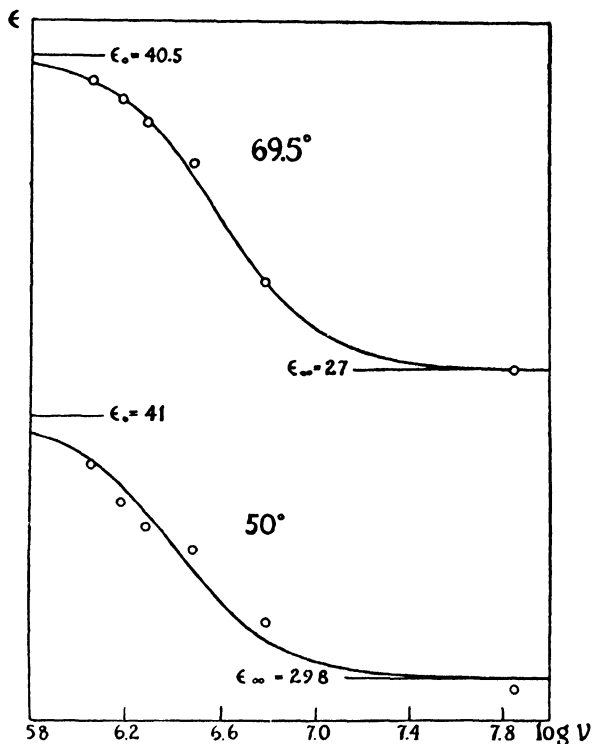


FIG. 5. The dielectric constant of a 4.2 per cent solution of zein in 70 per cent *n*-propyl alcohol as a function of frequency, ν . The smooth curves are calculated from equation 5.

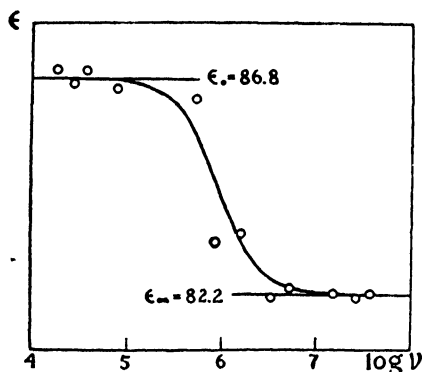


FIG. 6. The dielectric constant of a 0.4 per cent aqueous solution of hemoglobin as a function of frequency. The smooth curve is calculated from equation 5.

tion times should be proportional, are 0.017 and 0.034, respectively. If we assume the zein to have a molecular weight of 34,500 and to consist of spherical molecules, the relaxation times at the two temperatures calculated from Stokes' formula are 4.4×10^{-8} sec. and 9.2×10^{-8} sec., respectively, quite close to the experimental results. The values of the dielectric increments reckoned from the values of ϵ_0 and ϵ_∞ are approximately 12,000 at 69.5°C. and 10,000 at 50°C.

For comparison there are shown graphically in figure 6 Errera's results on a 0.4 per cent solution of hemoglobin in water at 13°C. The smooth curve corresponds to equation 5 with $\epsilon_0 = 86.8$, $\epsilon_\infty = 82.2$, and $x = 1.12 \times 10^{-6}$. The relaxation time corresponding to this value of x is close to 2×10^{-7} sec. on either interpretation of the dielectric constant. That calculated from Stokes' formula, taking account of the viscosity of the solution ($= 0.0118$ poise), on the basis of a molecular weight of 68,000 is 7.1×10^{-8} . Other results of Errera are fitted less closely by the theoretical curve, the region of dispersion extending in general over a longer range of frequency than is required by the simple theory, and the dielectric constant often showing an unexplained drop at the lowest frequencies.

REFERENCES

- (1) BLÜH: *Z. physik. Chem.* **106**, 341 (1923).
- (2) CAVALLARO: *Arch. sci. biol.* **20**, 567 (1934).
- (3) CAVALLARO: *Arch. sci. biol.* **20**, 583 (1934).
- (4) COHN, BERGGREN, AND HENDRY: *J. Gen. Physiol.* **7**, 81 (1924).
- (5) COHN: *Physiol. Rev.* **5**, 349 (1925).
- (6) COHN: *J. Am. Chem. Soc.* **56**, 784 (1934).
- (7) COHN: *Annual Review of Biochemistry*, Vol. IV, p. 93. Stanford University, California (1935).
- (8) DEVOTO: *Gazz. chim. ital.* **60**, 520 (1930).
- (9) DEVOTO: *Gazz. chim. ital.* **61**, 897 (1931).
- (10) DEVOTO: *Atti accad. Lincei* **14**, 432 (1931).
- (11) DEVOTO: *Gazz. chim. ital.* **63**, 50 (1933).
- (12) DEVOTO: *Gazz. chim. ital.* **63**, 119 (1933).
- (13) DEVOTO: *Gazz. chim. ital.* **63**, 247 (1933).
- (14) DEVOTO: *Gazz. chim. ital.* **63**, 491 (1933).
- (15) DEVOTO: *Z. physiol. Chem.* **222**, 227 (1933).
- (16) DEVOTO: *Gazz. chim. ital.* **64**, 76 (1934).
- (17) DEVOTO: *Gazz. chim. ital.* **64**, 371 (1934).
- (18) DEVOTO: *Z. Elektrochem.* **40**, 641 (1934).
- (19) DEVOTO: *Atti accad. Lincei* **19**, 50 (1934).
- (20) EBERT: *Z. physik. Chem.* **121**, 385 (1926).
- (21) EDSALL AND BLANCHARD: *J. Am. Chem. Soc.* **55**, 2337 (1933).
- (22) EDSALL AND WYMAN: *J. Am. Chem. Soc.* **57**, 1964 (1935).
- (23) ERRERA: *J. chim. phys.* **29**, 577 (1932).
- (24) EYRING: *Phys. Rev.* [2] **39**, 746 (1932).
- (25) FRANKENTHAL: *Z. physik. Chem.* **19**, 328 (1932).

- (26) FRANKENTHAL: *Z. physik. Chem.* **21**, 310 (1933).
- (27) FÜRTH: *Ann. Physik* **70**, 63 (1923).
- (28) GREENSTEIN, WYMAN, AND COHN: *J. Am. Chem. Soc.* **57**, 637 (1935).
- (29) GREENSTEIN AND WYMAN: *J. Am. Chem. Soc.* **58**, 463 (1936).
- (30) HAUSSER: *Sitzber. Heidelberg. Akad. Wiss.* **6** (1935).
- (31) HEDESTRAND: *Z. physik. Chem.* **135**, 36 (1928).
- (32) HUNTER AND PARTINGTON: *J. Chem. Soc.* **1933**, 87.
- (33) INGOLD: *Chem. Rev.* **15**, 225 (1934).
- (34) KIRKWOOD: *J. Chem. Physics* **2**, 351 (1934).
- (35) KUHN, W.: *Kolloid-Z.* **68**, 2 (1934).
- (36) KUHN, W.: *Z. physik. Chem.* **175A**, 1 (1935).
- (37) KUMLER: *J. Am. Chem. Soc.* **57**, 600 (1935).
- (38) LINDERSTRÖM-LANG: *Compt. rend. trav. lab. Carlsberg* **20**, No. 10 (1935).
- (39) MÜLLER, F. H.: *Trans. Faraday Soc.* **30**, 728 (1934).
- (40) ONSAGER: *J. Am. Chem. Soc.* **58**, 1486 (1936).
- (41) PAULING AND SHERMAN: *Proc. Natl. Acad. Sci.* **20**, 340 (1934).
- (42) PAULING: *J. Am. Chem. Soc.* **57**, 2705 (1935).
- (43) SHUTT: *Trans. Faraday Soc.* **30**, 893 (1934).
- (44) SMYTH: *Dielectric Constant and Molecular Structure*. The Chemical Catalog Co., Inc., New York (1931).
- (45) STUART, H. A.: *Molekülstruktur*. Julius Springer, Berlin (1934).
- (46) VAN ARKEL AND SNOEK: *Trans. Faraday Soc.* **30**, 707 (1934).
- (47) VICKERY AND SHORE: *Biochem. J.* **26**, 1101 (1932).
- (48) WALDEN AND WERNER: *Z. physik. Chem.* **129**, 389 (1927).
- (49) WYMAN: *Phys. Rev.* **35**, 623 (1930).
- (50) WYMAN: *J. Biol. Chem.* **90**, 443 (1931).
- (51) WYMAN: *J. Am. Chem. Soc.* **55**, 4116 (1933).
- (52) WYMAN: *J. Am. Chem. Soc.* **56**, 536 (1934).
- (53) WYMAN: *J. Am. Chem. Soc.* **58**, 1482 (1936).
- (54) WYMAN AND McMEEKIN: *J. Am. Chem. Soc.* **55**, 908 (1933).
- (55) WYMAN AND McMEEKIN: *J. Am. Chem. Soc.* **55**, 915 (1933).

INFLUENCE OF THE DIELECTRIC CONSTANT IN BIOCHEMICAL SYSTEMS

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INTRODUCTION

The dielectric constant presumably varies widely in biochemical systems. Urea, the amino acids and peptides, the proteins and the phospholipoids are known to increase the dielectric constant of even so polar a solvent as water. Fats, on the other hand, have low dielectric constants. All are important constituents of the body. The dielectric constant of different tissues may thus be expected to vary widely, depending upon the electrical properties of the molecular components.

Strong electrolytes are constituents of all biological systems, and so the dielectric properties of cells and tissues cannot be measured by existing methods. Instead it has been necessary to purify constituents of such systems until their conductivity was low, and then measure the dielectric constants of their solutions. Such measurements have now been made in a number of laboratories on a large number of amino acids and peptides, and the results, with widely different methods, are extremely concordant. Measurements upon amino acids and peptides, purified or synthesized by one or another of my collaborators, have been reported to you in the preceding paper by Wyman, and we can assume this knowledge in the following discussion. The measurements on egg albumin and hemoglobin made by Errera in Belgium have essentially been confirmed in our laboratory by Oncley, who is extending them to other proteins and to solvents of other dielectric constants.

The impetus to all this work came, of course, from the investigations of Debye. It had long been known that amino acids, peptides, and proteins were amphoteric electrolytes. In the same year in which Debye explained the behavior of strong electrolytes in terms of interionic forces, Bjerrum (3)—developing an idea that had previously been advanced by Bredig (8) and Adams (2)—demonstrated that amino acids, in the isoelectric condition, were not uncharged molecules, as had previously been assumed, but were what had been called zwitterions, and what for lack of a better

name, we shall call dipolar ions.¹ Although these neutral molecules have no net charge, and therefore do not move with the electric current, they bear equal numbers of positively and negatively charged groups on their surface. These dissociated groups give rise to electrostatic forces, which influence solvent molecules, other ions, and dipolar ions. It was to be hoped, therefore, that the development for dipolar ions of Debye's electrostatic force theory would offer fresh insight into the behavior of these important molecules. My colleagues, Scatchard and Kirkwood (34, 54), have both contributed to this aspect of the problem, and I shall leave to them its presentation, retaining for myself the task of describing the phenomena, whenever possible in quantitative terms, that need to be understood if we are to have an insight into systems containing many components,—some ions, some dipolar ions, and some uncharged molecules.

I. CHANGE IN FREE ENERGY WITH CHANGE IN SOLVENT

Born and Fajans in 1920 considered the change in free energy involved in the transfer of ions from an infinitely dilute gas to an infinitely dilute aqueous solution, and formulated an equation which may be written

$$\bar{F} - \bar{F}_{\text{gas}} = \frac{N\epsilon^2 z^2}{2b} \left(\frac{1}{D_0} - 1 \right) \quad (1)$$

in which ϵ is the elementary charge of the electron, z the valence of the ion, b its radius, and N Avogadro's number. If the transfer is from water to some medium other than a vacuum, which has the dielectric constant D , this expression becomes

$$\bar{F} - \bar{F}_0 = \frac{N\epsilon^2 z^2}{2b} \left(\frac{1}{D} - \frac{1}{D_0} \right) \quad (2)$$

Debye and McAulay (22) employed this equation in their study of mixed solvents. They followed Born in regarding the ions as electrical spheres of radius b . The solution outside this radius b was treated as continuous and of uniform dielectric constant.

The extension of this equation to the case of dipolar ions, although it has had a preliminary theoretical treatment (34, 54), has heretofore lacked an adequate experimental background. In recent studies we have estimated that part of the change in free energy due to electrostatic forces by comparing amino acids and peptides with comparable uncharged molecules (41, 42). Thus the logarithm of the solubility ratio—expressed as mole fraction in water, N_0 , and in ethanol, N_A —of glycine may be compared

¹ There is no adequate translation of the word "Zwitterion". We shall tentatively adopt the term "dipolar ion" introduced by Ingold, although it is not an ideal description of this class of molecules.

with glycolamide, of alanine with lactamide, and of norleucine with α -hydroxycaproamide (table 1). These amides of α -hydroxy acids have the same composition as, though different structures than, the α -amino acids. The comparison of solubilities in water and ethanol is somewhat unsatisfactory, however, because certain of the molecules are very soluble in water (43). Under these circumstances, solubility ratios may not yield activity

TABLE 1

Influence of dipolar ionization estimated by comparison of α -amino acids and α -hydroxy amides

α -AMINO ACIDS	$\log N_A/N_0$	AMIDES OF α -HYDROXY ACIDS	$\log N_A/N_0$	INFLUENCE OF DIPOLAR IONIZATION $\Delta \log N_A/N_0$
<i>Glycine</i> $\begin{array}{c} \text{H} \\ \\ +\text{H}_3\text{N}-\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \\ \\ \text{H} \end{array}$	-3.391	<i>Glycolamide</i> $\begin{array}{c} \text{H} \\ \\ \text{HO}-\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{NH}_2 \end{array} \\ \\ \text{H} \end{array}$	-0.799	-2.592
<i>Alanine</i> $\begin{array}{c} \text{H} \\ \\ +\text{H}_3\text{N}-\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \\ \\ \text{HCH} \\ \\ \text{H} \end{array}$	-2.856	<i>Lactamide</i> $\begin{array}{c} \text{H} \\ \\ \text{HO}-\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{NH}_2 \end{array} \\ \\ \text{HCH} \\ \\ \text{H} \end{array}$	-0.254	-2.602
<i>Norleucine</i> $\begin{array}{c} \text{H} \\ \\ +\text{H}_3\text{N}-\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array} \\ \\ (\text{HCH})_3 \\ \\ \text{HCH} \\ \\ \text{H} \end{array}$	-1.414	<i>α-Hydroxycaproamide</i> $\begin{array}{c} \text{H} \\ \\ \text{HO}-\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{NH}_2 \end{array} \\ \\ (\text{HCH})_3 \\ \\ \text{HCH} \\ \\ \text{H} \end{array}$	+1.084	-2.498

ratios. None the less, the solubility ratio N_A/N_0 is consistently from three hundred to four hundred times greater for the α -hydroxyamides than for the α -amino acids.

The comparison of amino acids and peptides with their hydantoic acids is more satisfactory, for, although the hydantoic acids prepared from them differ not only by the shift in proton characteristic of dipolar ion structure

TABLE 2

*Influence of dipolar ionization estimated by comparison of amino acids and peptides with hydantoic acids**

SUBSTANCE	LOG OF SOLUBILITY RATIO LOG N/N_0	INFLUENCE OF DIPOLAR IONIZATION
Formamide		
Glycine.....	-1.229	
Hydantoic acid.....	+0.755	-1.98
α -Aminocaproic acid.....	-0.360	
α -Aminocaproic hydantoic acid.....	+1.728	-2.09
Methanol		
Glycine.....	-2.515	
Hydantoic acid.....	-0.271	-2.24
α -Aminocaproic acid.....	-0.657	
α -Aminocaproic hydantoic acid.....	+1.568	-2.23
Ethanol		
Glycine.....	-3.391	
Hydantoic acid.....	-0.630	-2.76
α -Alanine.....	-2.856	
α -Alaninehydantoic acid.....	-0.139	-2.72
β -Alanine.....	-3.139	
β -Alaninehydantoic acid.....	-0.463	-2.68
α -Aminocaproic acid.....	-1.414	
α -Aminocaproic hydantoic acid.....	+1.352	-2.77
Diglycine.....	-4.367	
Diglycinehydantoic acid.....	-1.533	-2.83
Triglycine.....	-4.965	
Triglycinehydantoic acid.....	-2.253	-2.71
Butanol		
Glycine.....	-3.808	
Hydantoic acid.....	-1.011	-2.80
α -Aminocaproic acid.....	-1.711	
α -Aminocaproic hydantoic acid.....	+1.118	-2.83
Acetone		
Glycine.....	-4.401	
Hydantoic acid.....	-1.520	-2.88
α -Aminocaproic acid.....	-2.432	
α -Aminocaproic hydantoic acid.....	+0.437	-2.87

* These solubility data are reported in more detail in references 15, 41, and 42.

but also by a CONH group, this represents a constant difference estimated at +0.14 from comparison of glycolanide or lactamide with hydantoic acid and methylhydantoic acid. Diglycine is isomeric with methylhydantoic acid, that is, the hydantoic acid derived from α -alanine, as well as that from β -alanine. Their comparison is, however, not satisfactory, since both the CONH and the CH₂ groups require different amounts of work for their transfer, depending upon their position in the molecule (42). Comparison of a large series of amino acids and peptides with the hydantoic acids prepared from them (by treatment with potassium cyanate under the appropriate conditions) yields the consistent difference for the transfer from water to various other solvents shown in table 2. These studies suggest that, within the limits of error of the measurements, that part of the free energy of transfer from water to another solvent due to electrostatic forces is independent of the dipole moments of these molecules and of the

TABLE 3

Influence of CH₂ groups and of dipolar ion structure on change of free energy with change in solvent

SOLVENT	DIELECTRIC CONSTANT	INFLUENCE OF CH ₂ GROUPS		INFLUENCE OF DIPOLAR IONIZATION	
		log $\Delta N/N_0$	ΔF calc.	log $\Delta N/N_0$	ΔF calc.
Formamide	>84	+0.23	314	-2.03	-2768
Methanol	32.71	+0.44	600	-2.24	-3054
Ethanol	24.28	+0.49	668	-2.73	-3722
Acetone	20.83	+0.49	668	-2.87	-3913
Butanol	17.51	+0.53	723	-2.82	-3845
Heptanol	9.33	+0.53	723		

number of CH₂ groups in the paraffin chain. The result is the same if we compare glycine or norleucine, diglycine or triglycine, with their hydantoic acids. And the result is of the same order of magnitude whether the comparison is with hydantoic acids or α -hydroxyamides.

The same measurements may be employed in calculating the work involved in the transfer for each additional CH₂ group in paraffin chains ending in methyl groups.² This change in free energy has the opposite sign from that due to dipolar ionization and is the same whether the CH₂ groups are on uncharged molecules or dipolar ions.

The influences of CH₂ groups, and of dipolar ionization, upon the free energy of transfer to a variety of solvents estimated by comparison of α -amino acids and their derivatives are summarized in table 3.

² For CH₂ or CONH groups situated between polar groups the problem is far more complicated (42) and is not considered here.

These results are far simpler than could have been predicted on the basis of theoretical considerations. They do not reveal the expected influence of the dipole moments of the molecules on the free energy of transfer (34, 54), nor, in the case of the more soluble molecules, the influence of dipolar ions on each other in their saturated aqueous solutions. The latter effect has been estimated to be 0.15 for glycine in water from freezing-point measurements (55), and to be 0.13 from vapor-pressure measurements at 25°C. (57). Moreover, change in $\log N/N_0$ —or in $\Delta\bar{F}$ —is not proportional to the reciprocal of the dielectric constant. Thus the characterization of the solvent in terms of its dielectric constant is a less satisfactory approximation than in the case of ions.

When one considers that the electrostatic forces surrounding dipolar ions are of shorter range than those surrounding ions (34, 54), whereas their dimensions are far greater (11, 13), it is obvious that Coulomb forces cannot be expected as nearly to explain the behavior of dipolar ions as of ions. Among dipolar ions, those with electric moments large in comparison with their volumes behave most like ions, whereas those with moments small in comparison with the length of their paraffin side chains behave most like uncharged organic molecules.

Solubility in ethanol-water mixtures

Solubility in three-component systems is more complicated than in the two-component systems thus far considered. Besides the forces between solute molecules and the two solvent species, there are the forces between the solvent molecules themselves. Moreover, if the affinity of the solute is far greater for the one than for the other solvent, a redistribution of solvent molecules may occur in the neighborhood of solute molecules so that the solvent as a whole can no longer be considered a uniform medium.

None the less, studies upon amino acids, peptides, and their derivatives in ethanol-water mixtures illustrate many of the types of behavior with which we are concerned, and enable us to distinguish, at least qualitatively, between the forces due to the charged groups of dipolar ions and those due to the paraffin chain. When the logarithm of the solubility ratio of glycine and its peptides is plotted as ordinate against the mole fraction of ethanol in the solvent (figure 1) the three curves are very similar. All have steep segments at low mole fractions of alcohol, with comparable points of inflection in the range in which the solvent molecules are approximately equal in number. In systems containing larger amounts of ethanol the logarithm of the solubility may, as a first approximation, be considered to vary inversely as the mole fraction of ethanol. Straight lines have been drawn through these segments of the curves of glycine and its peptides.

The curves describing the behavior of formyl derivatives of the amino acids, their hydantoins and hydantoic acids in ethanol-water mixtures

(41, 42) also form a family, though their shape is quite different from that of the amino acids and peptides from which they were derived. For, whereas small amounts of alcohol diminish the solubility of α -amino acids and the peptides of glycine, they increase the solubility of their derivatives

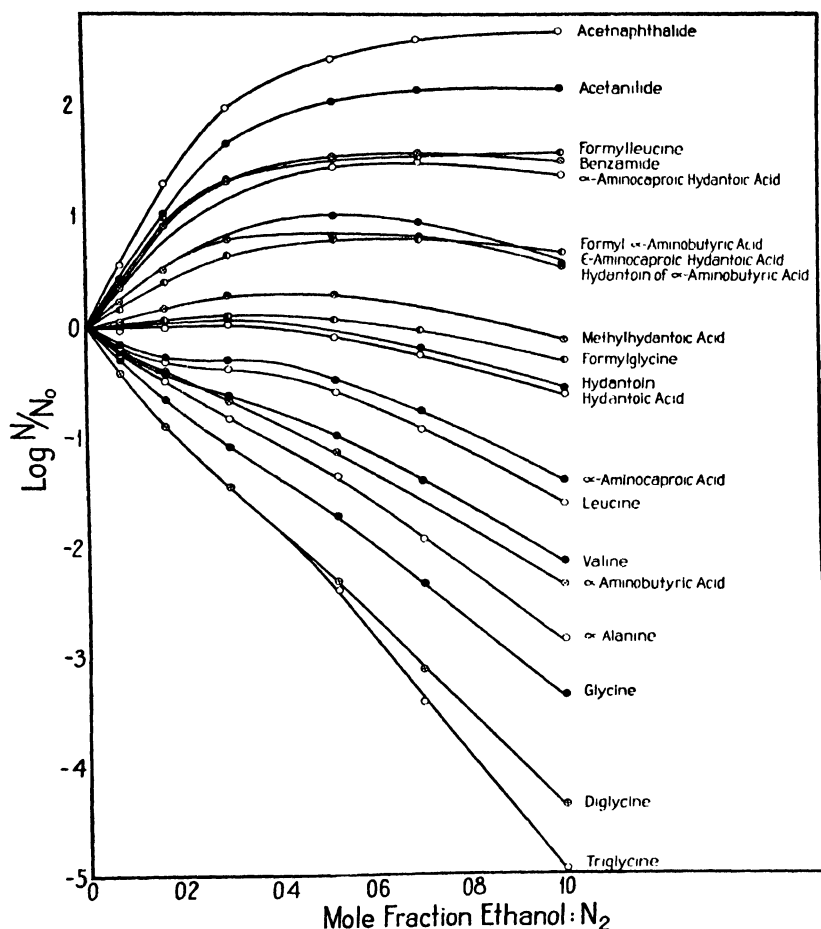


FIG. 1. Solubility of amino acids, peptides, and related substances in ethanol-water mixtures at 25°C.

which are no longer dipolar ions. This is particularly marked with α -aminocaproic hydantoic acid. The additional CH_2 groups of this molecule as compared with hydantoic acid are reflected by increased solubility in systems rich in ethanol. The curve for this substance is very similar to

that for formylleucine or benzamide (41) and such other typical organic compounds as acetanilide and acetnaphthalide. The isomer, ϵ -amino-caproic hydantoic acid, in which the CH_2 groups lie between polar groups, behaves far more like the formyl derivative or hydantoin of α -aminobutyric acid (42); that is to say, like a molecule with two less CH_2 groups. Its solubility in 80 per cent ethanol is approximately tenfold that in water and threefold that in ethanol, a type of behavior characteristic of a class of proteins, the prolamines.

All naturally occurring α -amino acids are less soluble in ethanol-water mixtures than in water.³ Whereas small amounts of ethanol greatly diminish their solubility, larger amounts have less effect the longer the paraffin side chains of the molecule (figure 1). Dipolar ions differing from each other only by the number of CH_2 groups in paraffin chains ending in methyl groups, n_{CH_2} , are related in their solubility behavior to glycine by the following approximate rule:

$$\log (N/N_0)_{\text{glycine}} = \log (N/N_0)_{\alpha\text{-amino acid}} - 0.49 v_2^2 n_{\text{CH}_2} \quad (3)$$

where all solubilities are given in mole fractions and v_2 is the volume fraction of ethanol in the solvent (41). In absolute alcohol the above equation reduces to the rule, and yields the value given in table 3. Whether the same rule with the coefficient characteristic of the other pure solvents studied will hold also for their mixtures with water remains to be investigated.⁴ It is also possible that comparable relations may obtain between various tripeptides and triglycine. In any case it would appear possible to analyze solubility ratios of α -amino acids in various solvents in terms of the charged groups and the length of the paraffin side chains in which they differ from each other. In these terms, also, one may hope to be able to analyze the behavior of still more complicated peptides, phospholipoids, and proteins.

II. CHANGE IN FREE ENERGY WITH CHANGE IN IONIC STRENGTH AND DIELECTRIC CONSTANT

The influence of neutral salts in increasing the solubility of proteins is so marked that it was observed in the middle of the last century. In 1859

³ The rules that have been deduced (table 3) demand that this should not be true for α -amino acids containing more than eight CH_2 groups, and measurements upon α -aminostearic acid demonstrate that it is far more soluble in ethanol than in water.

⁴ The logarithm of the ratio of solubility of α -amino acids in butanol saturated with water, to that in water (23), has a coefficient close to 0.4 for the CH_2 group, whereas the coefficient for formyl amino acids in pure butanol is 0.53. The volume fraction of butanol in a solution saturated with water is 0.835. Neglecting the effect of the amino acid on the solubility of water in butanol, and assuming the same equation to hold for butanol-water as for ethanol-water mixtures, we should have:

$$0.53 v_2^2 n_{\text{CH}_2} = 0.53 \times 0.835^2 n_{\text{CH}_2} = 0.37 n_{\text{CH}_2}$$

Denis, a French scientist, noted that certain of the proteins of the blood were insoluble in water, but soluble in dilute salt solutions. Proteins that behave in this way are classified as globulins. As a result of a study upon serum globulin in 1905 Mellanby concluded: "Solution of globulin by a neutral salt is due to forces exerted by its free ions. Ions with equal valencies, whether positive or negative, are equally efficient, and the efficiencies of ions of different valencies are directly proportional to the squares of their valencies" (44, p. 373). This accurate formulation of the principle of the ionic strength—rediscovered in 1921 by G. N. Lewis (38) as a description of the effects of neutral salts upon each other—acquired theoretical significance in Debye's theory of interionic forces. The ionic concentration, Γ , defined as the summation $\sum Cz^2$, where z is the valence of each ionic species, is related in Debye's theory to the temperature, the dielectric constant of the medium and κ , a measure of the thickness of the ion atmosphere, by the equation:

$$\kappa^2 = \frac{4\pi N\epsilon^2}{1000 DKT} \sum Cz^2 = \frac{12.67 \times 10^{18}}{DT} \quad (4)$$

The dielectric constant thus plays an important rôle in this theory in determining that part of the activity coefficients of ions due to Coulomb forces, *fe*.

$$-\log fe = \left(\frac{\epsilon^2 z^2}{2.303 \times 2DKT} \right) \left(\frac{\kappa}{1 + \kappa a} \right) \quad (5)$$

In this equation the dielectric constant is considered unaffected by change in ionic strength. If the dielectric constant of the medium also changes, a constant comparable to that employed by Debye and McAulay (22) and by Hückel (31) must also be added.

Since biological systems contain ions of various kinds as well as other components, some of which presumably decrease and others of which are known to increase the dielectric constant of water, the significance of these relations can scarcely be overemphasized. Were the interaction between dipolar ions and ions completely defined by the above equation, and were it necessary merely to substitute in equation 5 the change in the dielectric constants of solutions due to biological components in order to estimate the change in the activity coefficients of ions in biochemical systems, the problem would indeed be simple, at least in sufficiently dilute salt solutions. The influence of different ions would then depend upon their radii, b , their mean effective diameters, a , and valence, z , and the dielectric constant.

The Coulomb forces due to ions are not, however, the only ones which we must consider. The conditions in which the activity coefficients of ions and dipolar ions may be expected to depend most completely upon Coulomb forces will, however, be considered first. These obtain in media of

low dielectric constant at low temperatures. Conversely, the specific properties of ions and dipolar ions manifest themselves the more the higher the temperature and the dielectric constant.

In dilute solutions of electrolytes the logarithm of the activity coefficient is proportional to κ and to the square root of the ionic strength. In the case of dipolar ions the logarithm of the activity coefficient does not vary as the square root, but as the first power of the concentration. This was empirically discovered by studying the solvent action of neutral salts upon cystine, and theoretically demonstrated by Scatchard and Kirkwood (54) in an extension of the theory of Debye and Hückel to dipolar ions. They demonstrated that the term proportional to the square root of the concentration vanishes when the net charge is zero.

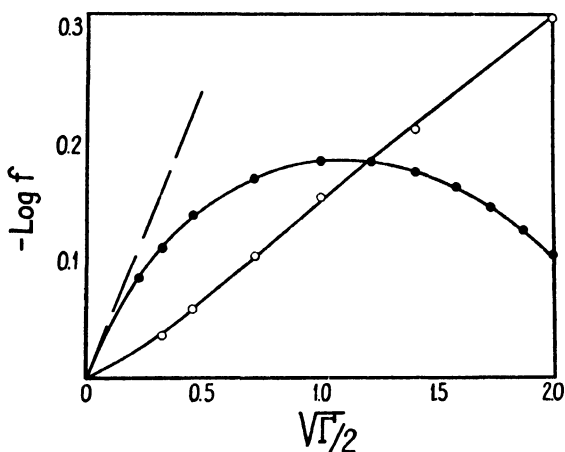


FIG. 2. Activity coefficients: ●, of sodium chloride (Harned and Nims: J. Am. Chem. Soc. **54**, 423 (1932)); ○, of cystine in sodium chloride.

The activity coefficients of cystine in the presence of sodium chloride, estimated by the solubility method, are compared with those of sodium chloride in the accompanying figure, so plotted as to demonstrate how completely this dipolar ion deviates from the square root law applicable to ions (figure 2). The activity coefficients of most amino acids cannot be determined in water by the solubility method because of their high solubility. The activity coefficients of glycine in sodium chloride solution have, however, been calculated by Scatchard and Prentiss (55) from freezing-point measurements and by Joseph (33) from electromotive force measurements at 1.4°C. in cells with amalgam electrodes, but without liquid junctions. The results of these two investigations are completely in accord and yield precise information regarding the influence of salt upon glycine and of glycine upon salt in aqueous solution.

Influence of sodium chloride upon glycine in media of varying dielectric constant

Most amino acids, peptides, and proteins are sufficiently insoluble in ethanol-water mixtures not to contribute appreciably to the dielectric constant of such solutions. Under these conditions the properties of the solutions approach those of the pure solvents. Glycine is soluble in water to the extent of 2.886 moles per liter. In 60 per cent ethanol its solubility is 0.157, in 80 per cent 0.0278, and in 90 per cent 0.0056 moles per liter (15).

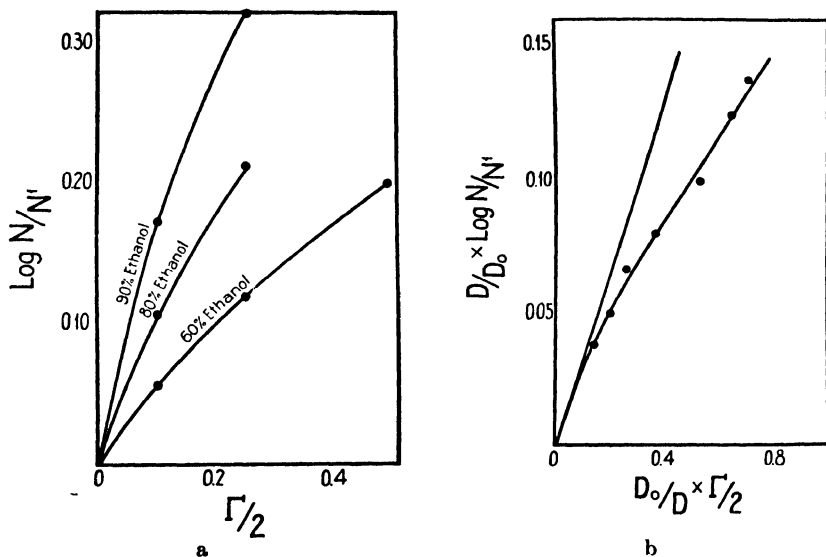


FIG. 3. Interaction of glycine in lithium chloride and ethanol-water mixtures: 3a, uncorrected; 3b, corrected for the influence on activity coefficients of the dielectric constant.

The solvent action of neutral salts upon glycine is greater the lower the dielectric constant of the medium. This is demonstrated if the ratio of the solubility in the ethanol-water mixture containing neutral salt, N , to that in the same ethanol-water mixture, N' , is plotted against the concentration of salt (figure 3a).

If the logarithm of the solubility ratio is multiplied by the dielectric constant ratio $[(D/D_0) \log N/N']$, and plotted against $(D_0/D) \Gamma/2$ the curves for glycine in 60, 80, and 90 per cent ethanol containing lithium chloride coincide within the limit of error of the measurements (figure 3b). We may, therefore, conclude that beyond 60 per cent ethanol changes in the activity coefficient of glycine with change in ionic strength are largely ascribable to Coulomb forces.

The addition of salt to an alcohol-water mixture increases the volume. Some decision must therefore be made as to the manner in which to compute the dielectric constant in the four-component systems here considered. Since dielectric constant measurements cannot be made in the presence of electrolytes, it remains an open question whether solutions would be more nearly isodielectric where the volume occupied by the salt is neglected, as well as any contribution of the salt to the dielectric constant, or whether the volume occupied by the salt should be considered to have the same properties as water and the sum of water plus salt be retained constant. Measurements have been made in systems constituted in both ways, and the solubility, computed in solvents defined in either way, yields the same results. All of the curves extrapolate to closely the same value for the limiting slope, which may be taken as 0.30 ± 0.02 regardless of the ethanol-water mixture, or of the method of defining the systems.

Influence of different alkali halides upon glycine

Kirkwood has developed an equation for the interaction between ions and dipolar ions and applied it to precisely these measurements upon glycine (34). In his equation the first term for the logarithm of the activity coefficient of a spherical dipolar ion increases with the square of its dipole distance R , divided by a , the sum of the radii of ion and dipolar ion. The greater the dipole moment the greater the solvent action of neutral salts. Moreover, if the center of the dipole be considered the center of the molecule, as in glycine and presumably many spherical proteins, this effect at low ionic strengths will dominate all others, since R^2 will be large in comparison with a .

The change in free energy is a very complicated function of the ionic strength in the Kirkwood equation, and this is especially true if the charged groups of dipolar ions are at the edge of the molecule. Under these circumstances the multipole moments cannot be neglected. If the limiting slope alone is considered, all terms up to the octopole moments being included, Kirkwood's expression may be written:

$$\begin{aligned} \frac{(D/D_0) \log f_e}{(D_0/D) \Gamma/2} = & -0.125 \frac{R^2}{a} \left\{ 1 + \frac{20}{27} \left(\frac{\rho}{a} \right)^2 \left[1 - \frac{R^2}{4\rho^2} \right] \right. \\ & \left. + \frac{7}{10} \left(\frac{\rho}{a} \right)^4 \left[1 - \frac{5R^2}{8\rho^2} + \frac{5R^4}{48\rho^4} \right] \right\} \quad (6) \end{aligned}$$

where ρ is the distance of the charged groups from the center of the molecule. The distance from the edge of the molecule, a value that is probably fairly constant for amino acids, peptides, and proteins, is therefore $(b - \rho)$.

Kirkwood's analysis of our curve for glycine yielded 10 A.U.² as an esti-

mate for R^2 or 3.17 A.U. for R . This is equivalent to a moment of 15×10^{-18} E.S.U. We have now studied the influence of other alkali halides on glycine, with the intention of varying this parameter in the above equation. Taking the radius of glycine to be 2.82 A.U. (13) and the radii of the salts, b , to be those estimated by Pauling (50), one obtains the estimates of $0.125/a$ shown in table 4. Assuming R^2 to be 10 A.U., the limiting slope of glycine in lithium chloride would be 0.32, in good agreement with our experimental findings. The studies upon sodium chloride and potassium chloride do not reveal lower but rather higher limiting slopes (0.31 ± 0.01) than for lithium chloride,⁵ and curvature is very similar, although, according to the theory, deviation from the limiting slope should be greater the larger the value of a .

TABLE 4
Sum of the radii of glycine and alkali halides

HALIDES	RADII OF IONS	SUM OF RADII OF GLYCINE AND IONS (2.82 + b)	0.125/ a
	b A.U.	a A.U.	
LiCl.....	1.082	3.90	0.0321
NaCl.....	1.231	4.05	0.0309
KCl.....	1.381	4.20	0.0298
LiBr.....	1.138	3.96	0.0316
NaBr.....	1.288	4.11	0.0304
KBr.....	1.438	4.26	0.0293
LiI.....	1.221	4.04	0.0309
NaI.....	1.370	4.19	0.0298
KI.....	1.520	4.34	0.0288

The radius of lithium chloride Pauling estimates to be the smallest among the alkali halides, and that of potassium iodide to be more than a third again as great, namely, 1.52 A.U. According to equation 6 the limiting slope should therefore be approximately 10 per cent smaller and the curvature should also reflect the larger value of a . The measurements upon the interaction of potassium iodide and glycine in ethanol (figure 4) reveal an appreciably lower limiting slope than in the case of sodium chloride or potassium chloride. The interaction of other alkali halides, as

⁵ In water, where these salts differ from each other far more in their influence upon amino acids and proteins, the solvent action of lithium chloride is greater than that of sodium chloride and that of sodium chloride than that of potassium chloride, and their salting-out effect is in the reverse order.

well as salts of other valence types with glycine and also with other amino acids and peptides, is being further investigated. Studies upon the influence of calcium chloride upon glycine in 80 per cent ethanol suggest that the solvent action of bi-univalent salts is greater than that of uni-univalent salts in this solvent as in water.

Influence of salt upon cystine

Most naturally occurring amino acids are less soluble in water than glycine; the imino acids proline and hydroxyproline are exceptions, as well as lysine and arginine, which are not α -amino acids. Solubility of amino acids in water is, as we have seen, generally decreased with increase

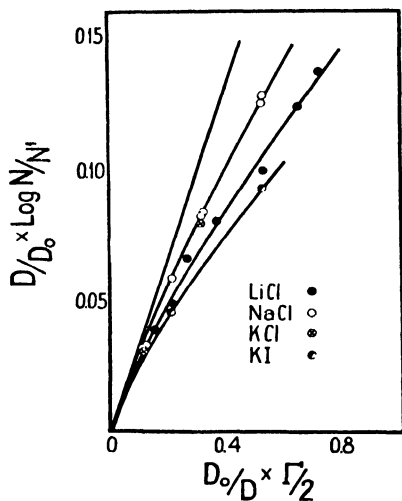


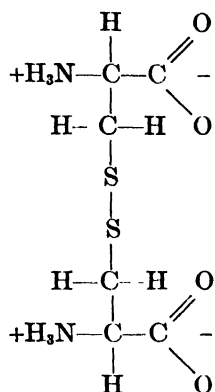
FIG. 4. Interaction of glycine and alkali halides in ethanol-water mixtures

in the number of CH_2 groups in the molecule. The longer the paraffin chain the greater the salting-out effect of neutral salts upon amino acids and this is greatest, as in the case of the proteins, for uni-bivalent salts, such as phosphates and sulfates and least, as has long since been shown by Pfeiffer and his collaborators (51), for bi-univalent salts, such as calcium chloride or strontium nitrate.

In order to determine the conditions under which the principle of the ionic strength—first described in connection with the solubility studies upon the proteins—obtains for amino acids, it seemed desirable to study a molecule which was relatively insoluble in water, but which possessed no long paraffin chains. For, the higher the solubility in water and therefore the dielectric constant of the medium, the smaller the Coulomb forces.

Conversely, the longer the paraffin chains of dipolar ions, the lower the dielectric constant of the medium must be for Coulomb forces to dominate the salting-out effect.

Cystine is the least soluble of the naturally occurring amino acids, having a solubility in water of 0.109 g. per liter at 25°C. It is a tetrapole, consisting essentially of two α -alanine molecules coupled by an S—S linkage.



Its electric properties might be expected to be determined by the configuration of the four charges constituting the two dipole pairs. Each of these may be expected to have moments comparable to that of glycine, but the vector sum of these moments might be zero or double that of glycine. The molal volume of cystine may be estimated to be 156 cc.⁶ and, considered as a sphere, its radius would therefore be 3.94 A.U.

The influence of calcium chloride upon the solubility of cystine was studied some years since by Blix (5). McMeekin has confirmed his measurements and studied the influence of a large number of other salts on the solubility of cystine in water (figure 5). The fan-like spread of solubility in the presence of different salts at the same ionic strength—multivalent cations having the greatest, and multivalent anions the smallest solvent action—resembles that characteristic of certain proteins and is considered in a later section of this paper.

The principle of the ionic strength can scarcely be said to be illustrated by salts in this medium at the concentrations studied. At the lowest calcium chloride concentrations studied by Blix, 0.063 mole per liter, the solubility is appreciably higher than at the same ionic strength of sodium chloride. The curvature in the case of the sodium chloride was, however,

⁶ Taking the S—S volume as 29.8 cc., as in α, α' -dithiodiacetic acid (30) and the volumes of the other groups as previously given (13).

far greater, and there was no evidence therefore that the limiting slopes would be different.

In order to determine the limiting slope more accurately the solvent action of sodium chloride on cystine was studied in 30 per cent ethanol. The results, very close to those of calcium chloride in water,⁷ suggest a limiting slope of 0.42, or something less than half again that of glycine. Assuming cystine to be a sphere, the sum of its radius, 3.94 A.U., and that of sodium chloride, 1.23 A.U. (50), yields a value of 5.17 A.U. for a . Taking 0.42 as the limiting slope for cystine in sodium chloride and putting it equal to R^2/a in Kirkwood's equation, R^2 is equal to 17.37 A.U. and R to 4.17 A.U. This calculation, though too simple, suggests that the two dipoles in cystine are neither parallel nor anti-parallel. They presumably

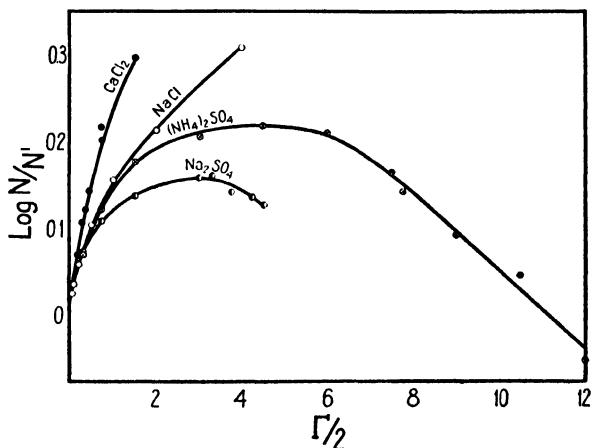


FIG. 5. Solubility of cystine in aqueous salt solutions

are at an angle with respect to each other as a result of rotation around the S—S bond. In order to study more exactly the influence of dipole moment upon the interaction with salts we therefore turned our attention to molecules in which the amino and carboxyl groups are separated by hydrocarbon and peptide chains.

Influence of salt upon peptides of varying dipole moment

The dipole moments of peptides increase with the number of amino acid residues bound in the chain. In the stretched condition the distance

⁷ Incomplete measurements upon cystine in 30 per cent ethanol containing calcium chloride suggest a slightly higher limiting slope of 0.48. If the salting-out constant K_s for cystine in sodium chloride, 0.14, be added to the apparent value, KR' , of 0.42, a still higher value of 0.56 is obtained for the true limiting slope, KR , and an estimate of R of 4.81 A.U. (See equation 8.)

separating the positive and the negative charge of these dipolar ions will therefore be greater for diglycine than for glycine, and for triglycine than for diglycine. Such molecules can, however, by no means be considered spherical. Rather they resemble cylinders of constant radius (13) and of the lengths estimated in table 5.

The peptides of glycine and the tetrapole lysylglutamic acid, which contains two negatively charged carboxyl and two positively charged

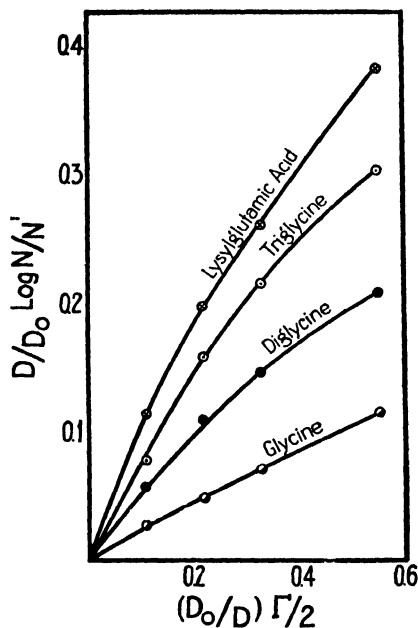


FIG. 6a

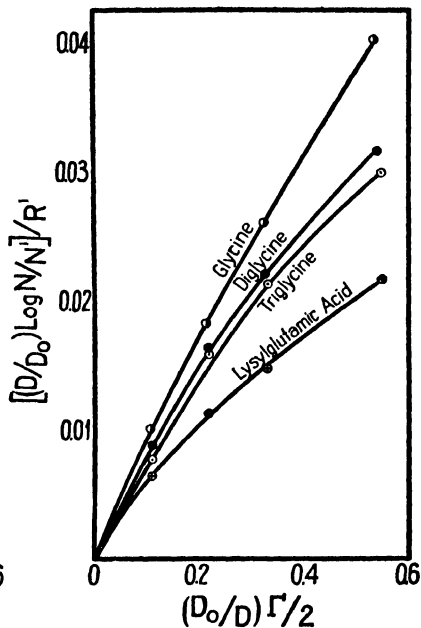


FIG. 6b

FIG. 6a. Solubility ratios, in 80 per cent ethanol containing sodium chloride, of amino acids and peptides.

FIG. 6b. Solubility ratios in 80 per cent ethanol containing sodium chloride, of amino acids and peptides divided by their dipole distances as estimated by structural considerations.

ammonium ions and has still larger electric moments (30), have been studied in 80 per cent ethanol containing sodium chloride at 25°C. The results are graphically represented in figure 6a, those for glycine being added for comparison. These measurements leave no doubt that the interaction of ions and dipolar ions is accompanied by greater change in free energy the greater the moments of the dipolar ions.

Although it is certain that the longer peptides have longer dipole moments, no satisfactory method is available for estimating the moments of

dipolar ions. In a recent discussion of the problem two approximations were compared (11). In the one the molecules are considered extended in solution, and the increment in the distance between the charged groups taken as 1.26 A.U. for each CH_2 group, and as 2.34 A.U. for each CONH group. Taking the dipole distance R of glycine as 3.17 A.U., that of diglycine is 6.67 and of triglycine 10.17. On this basis the longest dipole of lysylglutamic acid is 14.23 A.U., and the shorter one, which has the same configuration as diglycine, has a length in the direction of the chain of 3.5 A.U. The vector sum of these is therefore 17.73 A.U. (30).

The ratio $[(D/D_0) \log N/N']/R'$, where R' represents the estimated dipole distance in the stretched condition, is plotted in figure 6b against $(D_0/D) \Gamma/2$. The agreement at low concentrations of salt indicates that *the logarithms of the activity coefficients of amino acids and peptides are, as a first approximation, proportional to their dipole moments*. Moreover, these estimates of dipole distance may be considered maximal. Presumably there is at least some bending around the free bonds in these molecules, resulting in smaller dipole moments than these estimates, especially for the longer molecules.⁸ Eyring (25) and Kuhn (37) have estimated the amount of such bending from statistical considerations. Correcting for this effect would bring the peptide solubility curves, plotted as in figure 6b, still closer together and render the shapes of the molecules in solution rather elliptical than cylindrical.

Kirkwood has recently extended his treatment to an elliptical model and concluded that for long molecules the logarithm of the activity coefficient is proportional at low ionic strengths to R . Theory and experiment are thus in agreement that, for such molecules as the peptides that have thus far been studied, change in free energy with change in ionic strength due to Coulomb forces is proportional to the dipole distance R , whereas for spherical dipolar ions the limiting slope for a single dipole is proportional, according to Kirkwood's theory (34), to R^2/a .

Influence of salt upon proteins

Proteins, like the amino acids of which they are composed, vary with respect to their solubility in water, in alcohol-water mixtures, and in salt solutions. There is no reason to believe that the principles that apply in the case of amino acids do not hold also in the case of proteins, though the complexity of the analysis is of necessity far greater because of the vast size of the protein molecule, and the larger number of positively and negatively charged groups on its surface, even in the isoelectric condition. Whereas the radii of simple ions, considered as spheres, vary from 1.0 to 2.5 A.U.

⁸ The approach to this problem through the dielectric constant increments, δ , of dipolar ions is considered elsewhere in this paper.

and those of amino acids from 2.8 to approximately 4.0 A.U., the radius of egg albumin is estimated by Svedberg to be 22 A.U. (60), of hemoglobin 27 A.U., of edestin 39.5 A.U., and of the hemocyanin of *Helix* 120 A.U. (58). Certain proteins, among them the fibrinogen of blood (7), which is concerned with its coagulation, and the globulin of muscle, which is concerned with its contraction (46), far from being spherical, are rod-shaped, giving rise to double refraction of flow, the latter having a length that has been estimated⁹ at 6000 A.U.

A spherical protein is now best considered as a coiled polypeptide chain, held in its native form either by hydrogen bonds (45), by other forces between juxtaposed peptide linkages, or by electrostatic forces between its charged groups¹⁰ (14). Since the volumes of spheres increase with the third power of the radius, the effect of each protein molecule in displacing solvent is very great. The specific volumes of most proteins are close to 0.75.

The number of electric charges on most simple ions is one, two, three, or at most four or five. Egg albumin, a quite small protein, which is very soluble in water, but readily crystallizable from concentrated salt solutions, has approximately twenty-seven dissociable basic and twenty-seven dissociable carboxylic groups. Although the radius of egg albumin is approximately eight times that of the smallest amino acid, glycine, it has at least twenty-seven times as many charged groups.

It is not, however, the number of charged groups, but their distribution on the surface of molecules and the resultant electric moments that determine the solubility of amino acids, and presumably of proteins. The greater the electric moments of amino acids of equal crystal lattice energies, and the smaller the volume of non-polar groups in the molecule, the greater the solubility in water.

Hemoglobin, the iron-containing oxygen-combining protein of the blood, possesses a larger number of dissociable groups. It has approximately eighty-seven dissociable acid and an equal number of dissociable basic groups, but not more than seventy-five of these appear to form dipole pairs at the isoelectric point (12). Although the molecular weight of horse hemoglobin has been reported to be approximately equal, under certain conditions (9), to that of myoglobin and of egg albumin (58, 59), both

⁹ This estimate has been made by Edsall on the basis of measurements of double refraction of flow (46) and Werner Kuhn's theory (36).

¹⁰ From this point of view distortion of the native form occurs when protein is spread on a surface layer, and reveals the dimensions of the polypeptide chain (28, 32, 47). Increase in the heat motion in the case of these molecules or decrease in the dielectric constant of the medium leads also to denaturation, the resulting molecular configurations having far lower solubilities and presumably far smaller electric moments.

ultracentrifugal and osmotic-pressure measurements suggest that the normal molecular weight is 67,000 (1, 61). The molecular volume would therefore be 50,000 and the radius, calculated as a sphere, 27 A.U. Hemoglobin is, however, not as symmetrical a molecule as egg albumin (58).

The hemoglobin of the horse is soluble in water at 25°C. approximately to the extent of 17 g. per liter. In the presence of 1.05 moles of sodium chloride it is soluble to the extent of 198 g. per liter (29). Solubility is thus increased approximately tenfold by 1 mole of salt or to the extent characteristic of the influence "of a neutral salt upon a bi-bivalent or uni-quadrivalent compound" (17). The solubility of hemoglobin is thus so greatly increased by neutral salts as to warrant its characterization as a globulin. Its solubility in water is not sufficiently low, however, to demonstrate

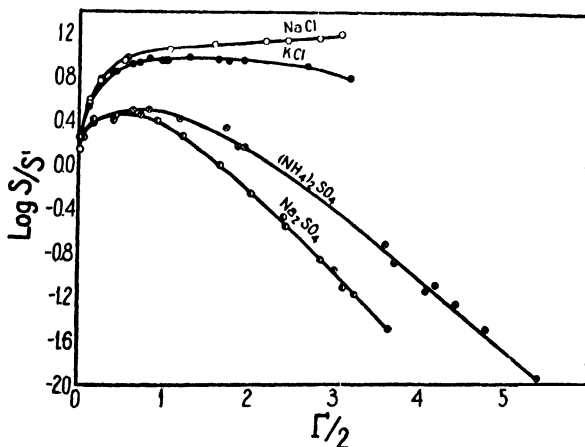


FIG. 7. Solubility of carboxyhemoglobin in aqueous salt solution

unequivocally the principle of the ionic strength under these conditions. For hemoglobin as for cystine the different solvent action of different salts is clearly demonstrated by the extensive investigations that have been carried on in aqueous solutions. The comparable nature of the salt effect upon amino acids and proteins is illustrated by figures 5 and 8. The curves in both cases have comparable contours, chlorides having the greatest solvent action of the salts studied, and the solvent action of the sulfates being overshadowed by their salting-out effect. In the case of hemoglobin, not only is the solvent action greater than in the case of cystine, but the salting-out effect becomes manifest at even lower concentrations. The serum globulin studied by Mellanby (44), which led him to formulate the principle of the ionic strength, had a far smaller solubility than hemoglobin, and the solvent action of neutral salts upon it was far greater.

Hemoglobin is sufficiently soluble to increase appreciably the dielectric constant of its saturated aqueous solutions. It therefore seemed desirable to determine its interaction with sodium chloride in a solvent of lower dielectric constant. The solubility of hemoglobin is estimated to be 0.036 g. per liter in 25 per cent ethanol at -5°C . (27). The logarithm of the ratio of its solubility in solutions containing salt to that in the salt-free ethanol-water mixture, multiplied by the dielectric constant ratio, is plotted in figure 8 against the sodium chloride concentration also multiplied by the dielectric constant ratio. Comparison with figure 7 demonstrates that the solvent action of sodium chloride is not only greater at the lower

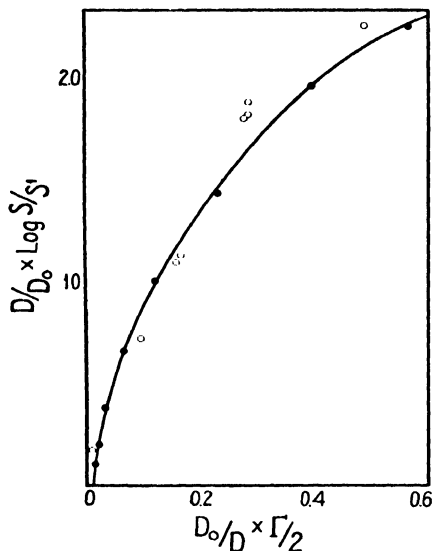


FIG. 8. Solubility ratio of carboxyhemoglobin in 25 per cent ethanol (●) compared with measurements (○) in aqueous solution (29) corrected by assuming 30,000 as the value of δ (48).

dielectric constant, but that it is greater even when the dielectric constant is corrected for, in the above manner. In order to account for the discrepancy one may assume that the solutions containing hemoglobin in water have a dielectric constant greater than that of water by approximately 30,000 per mole of hemoglobin.

The solubility measurements of Green (29) upon carboxyhemoglobin in aqueous sodium chloride, corrected on the assumption that the dielectric constant increment, δ , of this protein is 30,000 (figure 8) fall satisfactorily on the curve drawn through the points in 25 per cent ethanol, where the hemoglobin is too insoluble to contribute appreciably to the dielectric

constant of the solution. Nor is such a high value for δ fantastic. The dispersion curve upon this protein of Errera (6, 24), confirmed in our laboratory by Oncley (48), extrapolates to the slightly higher value of $35,000 \pm 5000$. The higher value of δ yields still greater estimates for $(D/D_0) \log S/S'$ in water. The dielectric constant of the most concentrated hemoglobin solution considered is on this basis 182 as compared with 87 in the absence of salt, and there is no present method of correcting the value of S' in water to the same dielectric constant as S . Moreover, a salting-out effect due to interaction with sodium chloride in solutions of high dielectric constant must, of course, also be assumed. These ten-

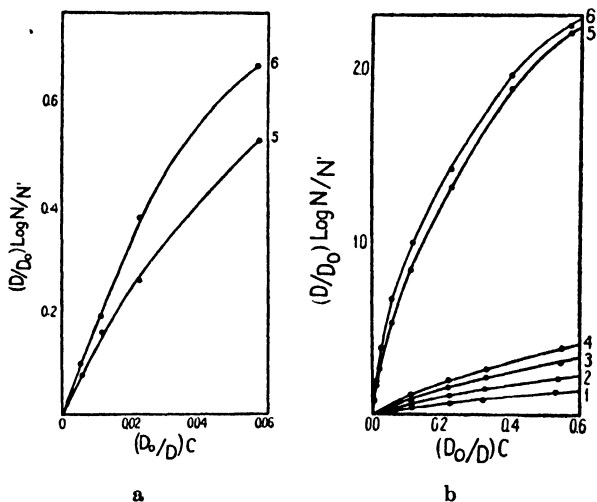


FIG. 9. Activity coefficients of: 1, glycine; 2, diglycine; 3, triglycine; 4, lysyl-glutamic acid; 5, egg albumin; and 6, carboxyhemoglobin in ethanol-water mixtures containing sodium chloride. (a) Proteins in dilute salt solutions. (b) More concentrated salt solutions, in which amino acids, peptides, and proteins have been studied.

tative calculations are presented as indicating the importance of the dielectric constant in influencing interaction with salts in concentrated protein solutions and presumably in biological systems.

Albumins are by definition water-soluble proteins. Forty per cent solutions of salt-free isoelectric egg albumin are readily prepared. Like other proteins, however, the solubility of egg albumin is greatly reduced by even small concentrations of ethanol. In 25 per cent ethanol at -5°C . (the same conditions that obtained in the hemoglobin study) the solubility of egg albumin was only 0.13 g. per liter. Under these conditions neutral salts increased its solubility many fold, as they do with globulins in aqueous solution.

The results upon egg albumin are also consistent with the prediction that in the interaction between ions and dipolar ions the logarithm of the solubility ratio is proportional to the ionic strength and not to its square root (27). At high salt concentrations, where Debye's law for ions would not be expected to hold, the logarithm of the solubility does, however, appear to vary with the square root of the ionic strength, as was noted in an earlier study (17). Only at concentrations lower than 0.02 is change in free energy proportional to change in ionic strength.

The measurements upon egg albumin in 25 per cent ethanol at -5°C . are plotted in figure 9a. This method of plotting has the advantage that it presumably yields that part of the activity coefficient due to Coulomb forces that also obtains in aqueous solution. It is conceivable that measurements upon egg albumin and hemoglobin at a lower dielectric constant would reveal even greater changes in solubility with change in ionic strength, and that the maximum slope has not been attained even at -5°C . in 25 per cent ethanol. The solubility of egg albumin falls off very rapidly with further increase in per cent of ethanol and has therefore rendered difficult the carrying out of measurements in such solvents.

Comparison of the shapes of the curves (figure 9b) for proteins with those for glycine, its peptides, and the tetrapole lysylglutamic acid, suggests that the general phenomenon is the same for amino acids, peptides, and proteins. The far greater influence of salts upon the latter suggests that they have far greater dipolar and multipolar moments. Their far greater size presumably accounts for the very rapid falling off of protein solubility curves from their limiting slopes with increase in salt concentration, though the distribution of charged groups will also influence curvature.

The study of peptides (16) led to the conclusion "that, as a first approximation, the logarithms of the activity coefficients of dipolar ions increase as the concentration of the salt, and the dipole distance." The peptides thus far studied are, however, roughly rod-shaped, whereas glycine, cystine, egg albumin, and hemoglobin are more nearly spherical molecules.

The egg albumin molecule may be considered roughly spherical. Its viscosity coefficient is close to that demanded by Einstein's equation (39, 18; see also Polson (52)). Its radius estimated as a sphere is 21.7 A.U. Adding 1.23 A.U. for the radius of sodium chloride yields a value of a of approximately 23 A.U. Were it sufficient to use only the first term of Kirkwood's equation for a single dipole in the case of a molecule containing twenty-seven positive and twenty-seven negative charges on its surface, the limiting slope 14, estimated from the interaction with sodium chloride, would give a value of 52 A.U. for R , or only slightly greater than the diameter of this protein (27).

Hemoglobin is not quite spherical according to Svedberg (58). The radius estimated by Einstein's law is 34 A.U., or considerably larger than

the 27 A.U. estimated on the assumption of a spherical molecule. Hemoglobin may thus be estimated to have a value of a between 28 and 35 A.U. Carrying out the same calculation on the basis of a limiting slope of 17 yields a value for R of from 62 to 69 A.U. In the case of this protein, as of egg albumin, the dipole distance estimated in this way is thus not far greater than the diameter of the molecule, and smaller even than if two parallel dipoles were at opposite edges of the molecule, although hemoglobin presumably has at least seventy-five dipole pairs.

The problem of the electrostatic forces between ions and such multipoles as the proteins has been considered by Kirkwood (35), who has tentatively concluded that they should not be treated as single dipoles. The first term of his equation for a spherical molecule should therefore not suffice, for it will give far too low an estimate of the summed electrical moments. The problem is further complicated in the case of the protein, since the charged groups are probably situated near the edge of the molecule. For glycine the diameter of the molecule is estimated to be 5.64 A.U. (13) and the dipole distance (34) 3.17 A.U. The difference, 2.47 A.U., may be considered the distance of the charged groups from the edge of the glycine molecule. Assuming the charged groups to be the same distance from the edge of protein molecules gives the maximum distance for a single dipole as 41 A.U. for egg albumin. Considering not only the limiting slope, but also the shape of the solubility curve (35), suggests that it is not the dipole, but the quadrupole and octopole moments that dominate the interaction of egg albumin with salt. Although studies of this kind should aid in our analysis of structure, the large number of charges involved preclude a unique solution of the distribution of the charges on the surface of the vast protein molecule.

Relation between dielectric constant increments of dipolar ions and their interaction with salts

There is as yet no satisfactory theory relating the dipole moments of polar molecules and the dielectric constants of their solutions. The present state of knowledge regarding this problem has been discussed in detail by others in this symposium, and will not therefore be considered here. (See Onsager (49) and Wyman (65).) The estimation of the electric moments of dipolar ions by their study in non-polar solvents has thus far not been possible. The molecules studied were insoluble in such solvents. Moreover they might be expected to pass over into their uncharged isomers under these conditions.

A modification of the classical theory for the case of polar solvents has recently been suggested by Wyman (64), according to which the dielectric constant increment per mole of solute is a nearly linear expression of the

polarization of solute molecules. According to it, and according to Debye's (20) relation between electric moment and polarization, δ is linear, not in the dipole moment but in its square. Werner Kuhn and Hans Martin (37) have also considered the problem of the shape of dipolar ions as revealed by dielectric constant measurements, and concluded that: "The electric moment and therefore the distance between the end groups of the molecules increase proportionately with the square root of the number of members in the chain . . . on the basis of statistical considerations" (37, p. 1528).

There is reason to believe that for dipolar ions of the same electric moment that part of the interaction with electrolytes which depends upon Coulomb forces is closely the same, regardless of the size of the molecule. Thus the solvent action of small concentrations of lithium chloride is closely the same for glycine and leucine in 90 per cent ethanol (10), whereas glycine is dissolved by low concentrations of sodium chloride in aqueous solution, and leucine, by virtue of its long paraffin chain, is salted out under the same conditions (51).

Not only is the interaction between dipolar ions and electrolytes for low concentrations of salt in regions of low dielectric constant closely the same for molecules having the same dipole distance, but the limiting slope,

$$[(D/D_0) \log N/N']/(D_0/D) \Gamma/2 = KR'$$

is greater the greater the dipole distance. This is readily demonstrated if we tentatively consider the square root of the dielectric constant increment proportional to the dipole distance and assume R for glycine to be 3.17 A.U. The quantity $\sqrt{\delta/2.3}$ then yields an estimate of the dipole distance R of molecules of known dielectric constant increment. The assumptions underlying this very rough approximation have been considered elsewhere in detail (11). The usefulness of the generalization and the close parallelism between the limiting slope and this quantity are given by the data in table 5. For the peptides studied the limiting slopes are approximately equal to $0.1 \sqrt{\delta/2.3}$. Although this relation does not hold in this form for the proteins that have been thus far investigated by these two methods, there is no doubt that it is the distribution of charges and the effective electrical moments of molecules that determine their influence both on the interaction between ions and dipolar ions and on the dielectric constant of solutions.

To the technical difficulties of measuring, and the theoretical difficulties of interpreting, the dielectric constant of solutions of other polar molecules, must be added, in the case of the proteins, the difficulty of employing sufficiently long wave lengths to overcome the anomalous dispersion due to these enormous molecules and of obtaining solutions of sufficiently low

conductivity. Indeed, earlier measurements suggested that solutions containing proteins had lower dielectric constants than water.

The difficulties of achieving conditions under which satisfactory measurements of the dispersion of proteins may be made have by now been largely overcome. Egg albumin and hemoglobin, as well as zein (62, 63), have been studied in more than one laboratory and the results, though not yet entirely concordant, are of the same order of magnitude and leave no doubt as to the approximate influence of proteins on the dielectric constant of solutions.

TABLE 5

Molecular volumes, number of dipole pairs, influence on dielectric constant, and interaction with salts of certain amino acids, peptides, and proteins

SUBSTANCE	MOLECULAR WEIGHT <i>M</i>	MOLECULAR VOLUME <i>V</i>	RADIUS OF SPHERICAL MOLECULES <i>b</i>	NUMBER OF DIPOLE PAIRS	LIMITING SLOPE $\left(\frac{(D/D_0) \log N/N'}{(D_0/D)C} \right)$ <i>KR'</i>	$\sqrt{\frac{\delta}{2.3}}$
Amino acids						
Glycine.	75.05	57.0	2.82	1	0.32	3.17
Leucine.	131.10	122.2	3.63	1	0.30	3.17
Cystine.	240.20	156.1	3.94	2	0.42†	†
Peptides						
Diglycine.	132.07	93.3	4.00*	1	0.58	5.51
Triglycine.	189.11	129.6	5.75*	1	0.8	7.02
Lysylglutamic acid. . . .	275.20	211.5	7.12*	2	1.2	12.25
Proteins						
Egg albumin.	34,000	25,500	21.7	27	14	$\begin{cases} 42 \\ 65 \end{cases}$
Hemoglobin (horse). . .	66,700	50,000	27.0	75	17	114

* One-half the lengths of these rod-shaped molecules, considered as cylinders.

† Too insoluble to study by this method.

‡ See footnote 7 and equation 8.

Errera (6, 24) reported measurements of the frequency variation of the dielectric constant for dilute aqueous solutions of several proteins, including egg albumin and hemoglobin. He estimated very low dielectric constants of between 4 and 5 for proteins in the solid state and dielectric constants of their aqueous solutions which yield values of δ of approximately 10,000 for egg albumin and 30,000 for hemoglobin.

The dielectric constants of aqueous solutions of isoelectric egg albumin have also been measured by Shutt (56) at 18°C. and at a frequency of 110 cycles per second. His results yield a value of approximately 4000. On-

cley (48), working in our laboratory on the same preparations of egg albumin and hemoglobin that were employed in the solubility studies, has essentially confirmed Shutt's values for δ for egg albumin and Errera's values for hemoglobin. Moreover, his results yield essentially the same estimates for the relaxation times of both proteins as those obtained by Errera. Measurements of the relaxation times of the same proteins by the methods of Malsch (40) and Debye (21) are being made simultaneously. The study of proteins by these diverse methods should result in accurate information regarding their relation to, and influence on, the dielectric constant.

Assuming that the dielectric constant increments for proteins also increase as the square of the mean dipole moment, and estimating R as the square root of δ , 2.3 yields 42 A.U. for egg albumin on the basis of Shutt's measurements and 65 on the basis of Errera's. Errera's value of 30,000 for δ leads to an estimate of 114 for the R of hemoglobin. The electric moments suggested by these estimates thus range from 200 to 550×10^{-18} E.S.U. These calculations suggest dipole moments which are of the same order as would result from single dipoles, or, at most, double dipoles situated at the opposite edge of these proteins. These results are thus consistent with those deduced from our solubility measurements, and suggest that the distribution of the charges on the surface of these proteins is such that the resultant moments are far smaller than they would be were all the dipole pairs on opposite sides of the molecule. None the less, these moments are far greater than those of any chemically well defined molecules that have thus far been investigated. It is largely as a result of these considerations that we have investigated the interactions of dipolar ions, and of ions with dipolar ions, in regions of high dielectric constant.

III. CHANGE IN FREE ENERGY IN SYSTEMS OF HIGH DIELECTRIC CONSTANT

In regions of high dielectric constant the interaction between ions and dipolar ions cannot be entirely described in terms of Coulomb forces. It is under these conditions that the principle of the ionic strength does not suffice to define the change in free energy of a dipolar ion even in dilute salt solutions, and that the specific properties of both ions and dipolar ions must be considered.

Systems containing more than one dipolar ion

Proteins, as well as phospholipoids, amino acids, and peptides, must ultimately be studied in the presence of one another if we are to understand the conditions that obtain in biochemical systems. The principles that have thus far been established are illustrated by the solubility of cystine in aqueous solutions of urea, amino acids, and the peptide diglycine.

The solvent action of neutral salts upon cystine has already been considered (figure 5). Glycine increases the solubility of cystine approximately to the same extent as sodium chloride (figure 10), although the solvent action in the case of the dipolar ion is smaller at low concentration and greater at high concentration.

At the same molar concentration α -aminobutyric acid has a much smaller influence than glycine in diminishing the activity coefficient—increasing the solubility—of cystine. It follows that in the interaction between dipolar ions not only their influence on the dielectric constant of solutions, but their specific chemical groups must be considered. The longer the paraffin chain, the smaller the influence of dipolar ions of the same electric moment in decreasing the activity coefficient of other dipolar ions, as of ions (26, 33). Moreover, diglycine, which has a larger dipole moment and

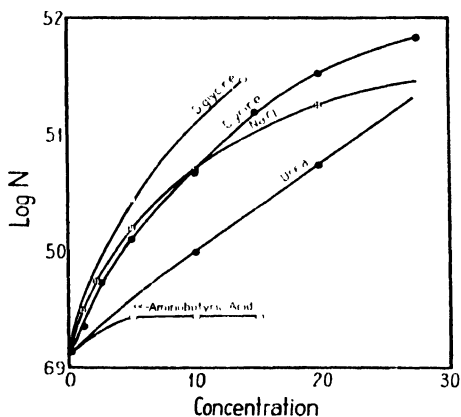


FIG. 10. Influence of various substances on solubility of cystine

in which all non-polar groups are between the charged ammonium and carboxyl groups (42), has a greater influence per mole than glycine, though a smaller influence than would be expected if the interaction of dipolar ions depended only on the dielectric constant of the solutions.

The solubility curves for cystine in glycine, diglycine, and α -aminobutyric acid would appear to belong to the same family, whereas the logarithm of the solubility of cystine is almost linear in the concentration of urea, suggesting a somewhat different mode of interaction between dipolar ions than between amino acids and urea. Although urea solutions have higher dielectric constants than water, the dielectric constant of even a saturated aqueous solution of urea is less than 100, or smaller than that of a molal solution of glycine, though the solvent action of this small polar molecule is far greater on both amino acids and proteins.

Systems containing concentrated electrolyte and more than one dipolar ion

If we now turn to systems containing three components—sodium chloride, cystine, and another dipolar ion—we have the changes in activity coefficient of the cystine indicated in figure 11. The solubility of cystine is changed far less by salt in systems containing amino acids or peptides than in aqueous solutions, or in solutions of still lower dielectric constant. The higher the concentration of the amino acid, the smaller the change in solubility due to the neutral salt. This might have been anticipated, since electrostatic forces are smaller the higher the dielectric constant.

Excepting in dilute salt solution the interaction with cystine varies considerably, depending on the nature of the dipolar ion employed in increas-

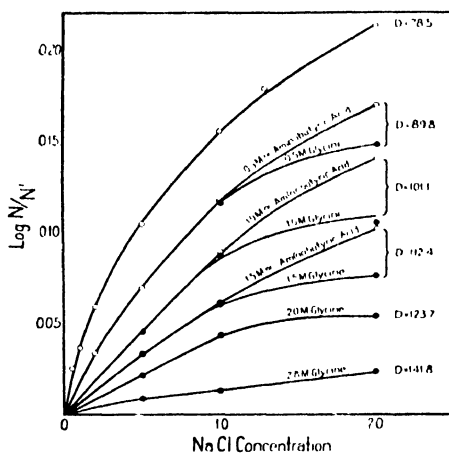


FIG. 11. Influence of amino acids on interaction between sodium chloride and cystine

ing the dielectric constant. Sodium chloride changes the free energy of cystine more in α -aminobutyric acid than in glycine solutions. This observation is related to two others. In the first place the activity coefficient of cystine is, as we have seen, decreased far more by glycine than by α -aminobutyric acid. In the second place, amino acids of longer hydrocarbon chain have a greater effect in increasing the activity coefficients of salts in concentrated salt solutions.

The influence of amino acids on sodium chloride has been estimated by the use of amalgam electrodes in cells without liquid junction (33). In sodium chloride solutions more concentrated than 1 molal, change in free energy of the electrolyte in the presence of amino acids has been shown to be approximately independent of electrolyte concentration, and the relations shown in table 6 obtain. The changes in the logarithm of the

activity coefficient of the amino acids (component 2) due to the salt (component 3) are calculated from E.M.F. measurements, according to the relation of Bjerrum (4).

$$\frac{\delta \log f_2}{m_3} = \nu \frac{\delta \log f_3}{m_2} \quad (7)$$

The results of this calculation yield values for the salting-out constants, K_s , of leucine in sodium chloride, in good agreement with that estimated from the solubility measurements of Pfeiffer and Würzler (51) as 0.09. The value of $K_{s\text{NaCl}}$ for α -aminobutyric acid we have determined to be 0.04 or just double the value, as deduced by equation 7, for the effect of the amino acid on the salt (33). Positive in sign, these activity coefficients indicate salting-out of the salt by the amino acid, and of the amino acid by the salt.

TABLE 6

Activity coefficients of amino acids and sodium chloride in concentrated salt solution

AMINO ACID	CHANGE IN LOG f OF NaCl DUE TO AMINO ACID. OBSERVED BY E.M.F. MEASUREMENTS	CHANGE IN LOG f OF AMINO ACID DUE TO NaCl CALCULATED FROM E.M.F. MEASUREMENTS	CHANGE IN LOG f OF AMINO ACID DUE TO NaCl. OBSERVED BY SOLUBILITY MEASUREMENTS
Glycine.....	0.01	0.02	
α -Alanine.....	0.01	0.02	
α -Aminobutyric acid.....	0.018	0.035	0.04
Valine.....	0.045	0.09	
Leucine.....	0.06	0.12	0.09

Systems containing dilute electrolyte and more than one dipolar ion

Interaction between electrolytes and dipolar ions takes place in biological systems at an ionic strength of approximately 0.16. The measurements reported in figure 11 indicate that at such salt concentrations glycine and α -aminobutyric acid have closely the same effect on the interaction between cystine and sodium chloride. This result suggests that *in sufficiently dilute salt solution the predominant effect of dipolar ions depends upon their influence on the dielectric constant of solutions and is largely independent of the nature of the dipolar ion*. Studies comparable to these have also been carried out in aqueous solutions of urea and diglycine.

Whereas decrease in activity coefficient due to Coulomb forces varies inversely as the second power of the dielectric constant, the increase in activity coefficient characteristic of both amino acids and proteins, and known as the salting-out effect, would appear to vary far less with temperature or dielectric constant. Any expression characterizing the behavior

of amino acids and proteins at high dielectric constant, even in dilute salt solution, must therefore contain a term opposite in sign from that due to Coulomb forces. For the case of cystine in systems containing sodium chloride and glycine, we may write for the limiting slope:

$$\frac{D}{D_0} \log \frac{N}{N'} = \left[KR - \frac{D}{D_0} Ks \right] \frac{D_0}{D} \frac{\Gamma}{2} = \left[0.56 - \frac{D}{D_0} 0.14 \right] \frac{D_0}{D} \frac{\Gamma}{2} \quad (8)$$

The value of Ks increases among dipolar ions of the same electric moment with the length of the paraffin side chain, whereas Coulomb forces, as we have seen, largely depend upon the dipole moment and only to a much smaller extent upon the radius of a molecule. The larger the number of non-polar groups in comparison with the dipole moment, the lower the dielectric constant must therefore be in order that the change in free energy with change in ionic strength may yield an estimate of Coulomb forces. Conversely, the higher the dielectric constant the smaller the first term in such an expression becomes, and the more accurately Ks can be estimated.

The very small solvent action of low concentrations of sodium chloride upon cystine is approximately accounted for by assuming the value 0.14 for Ks of cystine in such systems. This value for this constant may also be calculated by means of an approximate expression of Kirkwood's (35; and see equation 28 in reference 11) developed for spherical molecules without distinguishing in its tentative form between dipolar ions with paraffin chains and those in which the CH_2 groups are largely between polar groups. It yields somewhat lower values for tyrosine and higher values for glycine and most proteins than those observed in concentrated salt solutions.¹¹

The salting-out effect may be considered as due at least in part to the fact that a dipolar ion "displaces a certain quantity of solvent and therefore reduces the polarization of the solvent by the salt ion" (35). The studies that have thus far been carried out in media of high dielectric constant indicate that such polarization effects will play a large rôle even in dilute salt solutions. Under these circumstances differences in the polarizability due to different ions will manifest themselves in biological systems, as well as differences due to the non-polar groups and dipole moments of

¹¹ Values of Ks measured in concentrated salt solutions would appear to be lower than those estimated as the difference between measurements in dilute salt solution and the expectation from Coulomb forces. In comparison with the value 0.14, given above, Ks of cystine in concentrated ammonium sulfate solution (figure 5) is 0.05. Comparably, the limiting slope determined for glycine in dilute aqueous sodium chloride by E.M.F. measurements is 0.24 (33), or approximately 0.08 less than in media of low dielectric constant, in good agreement with the value 0.06 calculated by Kirkwood's equation (35).

dipolar ions. The forces concerned would appear, however, not to be very different from those considered by Debye (19, 22) and others (31, 53) for the change in free energy of electrolytes in the presence of other electrolytes and non-electrolytes. Systematic studies may be expected to analyze in these terms also the interactions between salts, amino acids, and proteins in regions of high dielectric constant.

REFERENCES

- (1) ADAIR, G. S.: *Proc. Roy. Soc. London* **120A**, 573 (1928).
- (2) ADAMS, F. Q.: *J. Am. Chem. Soc.* **38**, 1503 (1916).
- (3) BJERRUM, N.: *Z. physik. Chem.* **104**, 147 (1923).
- (4) BJERRUM, N.: *Z. physik. Chem.* **104**, 406 (1923).
- (5) BLIX, G.: *Z. physiol. Chem.* **178/179**, 109 (1928).
- (6) BLOCH, B. M., AND ERRERA, J.: *Physik. Z.* **33**, 767 (1932).
- (7) BOEHM, G., AND SIGNER, R.: *Helv. Chim. Acta* **14**, 1370 (1931).
- (8) BREDIG, G.: *Z. Elektrochem.* **6**, 33 (1899).
- (9) BURK, N. F., AND GREENBERG, D. M.: *J. Biol. Chem.* **137**, 197 (1930).
- (10) COHN, E. J.: *Naturwissenschaften* **20**, 663 (1932).
- (11) COHN, E. J.: *Annual Review of Biochemistry*, Vol. IV, p. 93. Stanford University (1935).
- (12) COHN, E. J., GREEN, A. A., AND BLANCHARD, M. H.: *In press*.
- (13) COHN, E. J., McMEEKIN, T. L., EDSALL, J. T., AND BLANCHARD, M. H.: *J. Am. Chem. Soc.* **56**, 784 (1934).
- (14) COHN, E. J., McMEEKIN, T. L., EDSALL, J. T., AND BLANCHARD, M. H.: *J. Biol. Chem.* **100**, Proc. xxviii (1933).
- (15) COHN, E. J., McMEEKIN, T. L., EDSALL, J. T., AND WEARE, J. H.: *J. Am. Chem. Soc.* **56**, 2270 (1934).
- (16) COHN, E. J., McMEEKIN, T. L., GREENSTEIN, J. P., AND WEARE, J. H.: *J. Am. Chem. Soc.* **58**, 2365 (1936).
- (17) COHN, E. J., AND PRENTISS, A. M.: *J. Gen. Physiol.* **8**, 619 (1927).
- (18) DANIEL, J., AND COHN, E. J.: *J. Am. Chem. Soc.* **58**, 415 (1936).
- (19) DEBYE, P.: *Z. physik. Chem.* **130**, 56 (1927).
- (20) DEBYE, P.: *Polar Molecules*. The Chemical Catalog Co., Inc., New York (1929).
- (21) DEBYE, P.: *Trans. Faraday Soc.* **30**, 679 (1934).
- (22) DEBYE, P., AND MCAULAY, J.: *Physik. Z.* **26**, 22 (1925).
- (23) ENGLAND, A., JR., AND COHN, E. J.: *J. Am. Chem. Soc.* **57**, 634 (1935).
- (24) ERRERA, J.: *J. chim. phys.* **29**, 577 (1932).
- (25) EYRING, H.: *Phys. Rev.* [2] **39**, 746 (1932).
- (26) FAILEY, C. F.: *J. Am. Chem. Soc.* **54**, 576 (1932); **54**, 2367 (1932); **55**, 4374 (1933).
- (27) FERRY, R. M., COHN, E. J., AND NEWMAN, E. S.: *J. Biol. Chem.* **114**, Proc. 34 (1936); *J. Am. Chem. Soc.* **58**, 2370 (1936), and unpublished data.
- (28) GORTER, E.: *Verhand. Akad. Wetenschappen Amsterdam* **29**, 1262 (1926); **34**, 1257 (1926); **36**, 922 (1933); **37**, 20 (1934); **37**, 355 (1934).
- (29) GREEN, A. A.: *J. Biol. Chem.* **93**, 495 (1931); **93**, 517 (1931); **95**, 47 (1932).
- (30) GREENSTEIN, J. P., WYMAN, J., JR., AND COHN, E. J.: *J. Am. Chem. Soc.* **57**, 637 (1935).
- (31) HÜCKEL, E.: *Physik. Z.* **26**, 93 (1925).
- (32) HUGHES, A. H., AND RIDEAL, E. K.: *Proc. Roy. Soc. London* **137A**, 62 (1932).

- (33) JOSEPH, N. R.: Studies on the Interaction of Amino Acids and Strong Electrolytes, Thesis, Harvard University (1934); *J. Biol. Chem.* **111**, 479, 489 (1935).
- (34) KIRKWOOD, J. G.: *J. Chem. Physics* **2**, 351 (1934).
- (35) KIRKWOOD, J. G.: Personal communication.
- (36) KUHN, W.: *Kolloid-Z.* **62**, 269 (1933); *Z. physiol. Chem.* **161**, 1, 427 (1932).
- (37) KUHN, W., AND MARTIN, H.: *Ber.* **67**, 1526 (1934).
- (38) LEWIS, G. N., AND RANDALL, M.: *J. Am. Chem. Soc.* **43**, 1112 (1921).
- (39) LOEB, J.: *J. Gen. Physiol.* **4**, 73 (1921-22).
- (40) MALSCH, J.: *Ann. Physik* **12**, 865 (1932); *Physik. Z.* **33**, 19 (1932).
- (41) McMEEKIN, T. L., COHN, E. J., AND WEARE, J. H.: *J. Am. Chem. Soc.* **57**, 626 (1935).
- (42) McMEEKIN, T. L., COHN, E. J., AND WEARE, J. H.: *J. Am. Chem. Soc.* **58**, 2173 (1936).
- (43) McMEEKIN, T. L., COHN, E. J., AND WEARE, J. H.: Unpublished data.
- (44) MELLANBY, J.: *J. Physiol.* **33**, 338 (1905).
- (45) MIRSKY, A. E., AND PAULING, L.: *Proc. Natl. Acad. Sci.* **22**, 439 (1936).
- (46) MURALT, A. V., AND EDSELL, J. T.: *J. Biol. Chem.* **89**, 315, 351 (1930).
- (47) NEURATH, H.: *J. Phys. Chem.* **40**, 361 (1936).
- (48) ONCLEY, J. L.: Personal communication.
- (49) OSBAGER, L.: *J. Am. Chem. Soc.* **58**, 1486 (1936).
- (50) PAULING, L.: *J. Am. Chem. Soc.* **50**, 1036 (1928).
- (51) PFEIFFER, P., AND WÜGLER, J.: *Z. physiol. Chem.* **97**, 128 (1916).
PFEIFFER, P., AND ANGERN, O.: *Z. physiol. Chem.* **133**, 180 (1924).
- (52) POLSON, A.: *Nature* **137**, 740 (1936).
- (53) SCATCHARD, G.: *Chem. Rev.* **3**, 383 (1927); *Trans. Faraday Soc.* **23**, 454 (1927).
- (54) SCATCHARD, G., AND KIRKWOOD, J. G.: *Physik. Z.* **33**, 297 (1932).
- (55) SCATCHARD, G., AND PRENTISS, S. S.: *J. Am. Chem. Soc.* **56**, 1486, 2314 (1934).
- (56) SHUTT, W. J.: *Trans. Faraday Soc.* **30**, 893 (1934).
- (57) SMITH, L. R. B., AND SMITH, P. K.: *J. Biol. Chem.* **117**, 209 (1937).
- (58) SVEDBERG, T.: *Kolloid-Z.* **51**, 10 (1930).
- (59) SVEDBERG, T.: *Kolloid-Z.* **67**, 2 (1934).
- (60) SVEDBERG, T., AND NICHOLS, J. B.: *J. Am. Chem. Soc.* **48**, 3081 (1926).
- (61) SVEDBERG, T., AND NICHOLS, J. B.: *J. Am. Chem. Soc.* **49**, 2920 (1927).
- (62) WATSON, C. C., ARRHENIUS, S., AND WILLIAMS, J. W.: *Nature* **137**, 322 (1936).
- (63) WYMAN, J., JR.: *J. Biol. Chem.* **90**, 443 (1931).
- (64) WYMAN, J., JR.: *J. Am. Chem. Soc.* **56**, 536 (1934).
- (65) WYMAN, J., JR.: *J. Am. Chem. Soc.* **58**, 1482 (1936).

STATISTICAL MECHANICS OF LIQUID SOLUTIONS¹

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I. INTRODUCTION

In the formulation of a molecular theory of solutions, there are two main problems to be considered. The first is the calculation of intermolecular forces from a knowledge of molecular structure, and the second is the correlation of the macroscopic properties of a thermodynamic system with the behavior of a dynamical system, consisting of many molecules executing thermal motion under known intermolecular and external forces. In the calculation of certain types of intermolecular force, for example, between ions and between molecules containing low-frequency electric multipole moments, simple electrostatics suffice. A more comprehensive theory of intermolecular forces is furnished by quantum mechanics. The nature of van der Waals forces between non-polar molecules and of the repulsive forces, which determine molecular size, is now well understood. It is true that computational difficulties stand in the way of exact calculations for all but the simplest molecules. Nevertheless, rather good approximations to the potential of van der Waals force can be obtained in terms of a few simple molecular constants, such as polarizability and ionization potential. What is perhaps more important, the approximate form of the potential of intermolecular force as a function of the molecular coordinates is known.

In the present article, we shall be chiefly concerned with the second problem, which lies within the province of statistical mechanics. In the study of liquids at ordinary temperatures it is usually sufficient to use classical statistical mechanics. This is permissible when the motion of

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the molecules involves only a high frequency and a low frequency type, in the sense of van Vleck's definition. The high frequency type of motion is characterized by the fact that the interval between adjacent energy levels is large relative to kT , the product of Boltzmann's constant and the absolute temperature. Under these circumstances there is no appreciable thermal excitation above the lowest energy state. The low frequency type of motion, on the other hand, is characterized by energy intervals very small relative to kT . The internal motion, electronic and vibrational, of most molecules is of the high frequency type at ordinary temperatures, while the translational and rotational motion is of the low frequency type.

In an earlier article (11) a method for the statistical treatment of liquids was developed on the basis of the classical canonical ensemble. This method provides a suitable basis for the formulation of a general theory of solutions. In addition to yielding a number of new results, it embraces those of older special theories as parts of a unified whole. Both electrolytes and non-electrolytes fit naturally into the scheme. We shall undertake the formulation of the theory as well as a discussion of some of its applications, particularly to electrolyte solutions. While there still remain a number of obstacles to be overcome, the theory is at present sufficiently well developed to yield some interesting results.

II. GENERAL THEORY

The Helmholtz free energy F_N of a liquid solution consisting of N molecules is related to the potential of intermolecular force, V_N , by the method of the canonical ensemble, in the following manner

$$e^{-\beta F_N} = \left[\prod_{s=1}^r \frac{f_s(T)^{N_s}}{N_s!} \right] Z_N$$

$$Z_N = \int \dots \int e^{-\beta V_N} dv_1 \dots dv_N \quad (1)$$

where β is equal to $1/kT$, and N_1, \dots, N_r are the numbers of molecules of the several components of the solution. The function $f_s(T)$ is a product of the internal partition function of a molecule of type s and the classical momentum phase integral associated with its low frequency translational and rotational degrees of freedom. The familiar phase integral Z_N extends over the translational and rotational configuration space of each molecule, bounded by the volume v of the solution. We denote by dv_i a differential element of this configuration space, divided by 4π for diatomic molecules and linear polyatomic molecules or by $8\pi^2$ for non-linear polyatomic molecules.

It has been previously shown (11) that the chemical potential of a component i of the solution may be expressed in the form

$$\mu_i = -kT \log \left[\frac{f_i(T)}{N_i} \frac{Z_N}{Z_{N-i}} \right] \quad (2)$$

where Z_{N-i} is the phase integral of the system with a single molecule of type i removed, the temperature, volume, and numbers of molecules of the remaining components being the same as in Z_N . We suppose that the potential of intermolecular force may be represented as the sum of terms V_{ik} , each depending upon the relative coördinates of a single molecular pair

$$V_N = \sum_{\substack{i=1 \\ i < k}}^N V_{ik} \quad (3)$$

This is no real restriction on the method, for it may be easily extended to include terms V_{ikl} depending upon the coördinates of three molecules, and so on. For simplicity, we shall not include such terms. In treating chemically saturated molecules, terms of the form V_{ikl} are probably needed only when it is desired to take account of the induced or optical polarization of molecules in a system containing ions or dipoles. Such interactions are usually unimportant in comparison with other intermolecular forces. The form of equation 3 might be questioned for the repulsive forces, which operate at small intermolecular distances and determine molecular size. However, these repulsive forces generally act in such a manner as to make the molecules behave as hard impenetrable objects. Thus their rôle consists in making $e^{-\beta V}$ vanish whenever the relative coördinates of any molecular pair are within the region of repulsion. This may be accomplished with a potential of the form of equation 3, in which each V_{ik} assumes a large value V_R whenever the relative coördinates of the pair are within the region of repulsion of volume ω_{ik} . Strictly speaking, V_R should be infinite, but for practical purposes it is only necessary to assume it very large relative to kT , a procedure which avoids a certain amount of mathematical hedging.

It is convenient to introduce a fictitious potential

$$\begin{aligned} V_N(\lambda_i) &= V_{N-1} + \lambda_i V_i \\ V_i &= \sum_{k=1}^N V_{ik} \end{aligned} \quad (3a)$$

where λ_i is an arbitrary parameter, and V_{N-1} is the potential of intermolecular force in a system containing one less molecule of type i than the original one. Corresponding to $V_N(\lambda_i)$ we may construct a phase integral

$Z_N(\lambda_i)$ which is equal to Z_N when λ_i has the value unity and to Z_{N-i} when λ_i is zero. Following the methods of the earlier paper (11), we finally obtain for the chemical potential of the component i

$$\begin{aligned}\mu_i &= kT \log N_i/v + \sum_{k=1}^r \frac{N_k}{v} (J_{ik} + G_{ik}) + \varphi_i(T) \\ J_{ik} &= \int_0^1 \int_0^{\omega_{ik}} V_{ik} e^{-\beta W_i^k(\lambda_i)} dv_k d\lambda_i \\ G_{ik} &= \int_0^1 \int_{\omega_{ik}}^v V_{ik} e^{-\beta W_i^k(\lambda_i)} dv_k d\lambda_i \\ \varphi_i(T) &= -kT \log f_i(T)\end{aligned}\quad (4)$$

where the integral J_{ik} extends only over the region of repulsion ω_{ik} , and G_{ik} extends over the rest of the volume of the solution. The function $W_i^k(\lambda_i)$ is the potential of average force between i and k , defined as follows

$$e^{-\beta W_i^k(\lambda_i)} = \frac{v \int \dots \int e^{-\beta V_N(\lambda_i)} dv_1 \dots dv_{N-2}}{\int \dots \int e^{-\beta V_N(\lambda_i)} dv_1 \dots dv_{N-1}} \quad (5)$$

where the integral in the numerator extends over all molecules except i and k , while that in the denominator extends over all molecules except i . In the earlier article (11) it is shown that $W_i^k(\lambda_i)$ satisfies the following equation

$$W_i^k(\lambda_i) = \lambda_i V_{ik} + \sum_{l=1}^r \frac{N_l}{v} \int_0^{\lambda_i} \int_0^v V_{il} (e^{-\beta W_{ik}^l(\lambda_i)} e^{-\beta W_i^l(\lambda_i)} - 1) dv_l d\lambda_i \quad (6)$$

where $W_{ik}^l(\lambda_i)$ is the potential of average force acting on a molecule l in the neighborhood of the fixed pair i and k . It is defined by a relation similar to equation 5. A set of integral equations for the $W_i^k(\lambda_i)$ of the several types of pairs in the solution may be obtained if $W_i^l(\lambda_i)$ is approximated by $W_i^l(\lambda_i) + W_k^l(1)$:

$$W_i^k(\lambda_i) = \lambda_i V_{ik} + \sum_{l=1}^r \frac{N_l}{v} \int_0^{\lambda_i} \int_0^v V_{il} e^{-\beta W_i^l(\lambda_i)} (e^{-\beta W_k^l(1)} - 1) dv_l d\lambda_i \quad (7)$$

The nature of the superposition approximation, upon which this equation is based, has been discussed elsewhere (11). It may happen that outside the regions of repulsion, βW_i^l and βW_k^l are small enough to permit expansion of the exponentials with the neglect of terms in the second and higher powers of β . When this is done a set of approximate linear integral equations is obtained,

$$\begin{aligned}
 W_i^k(\lambda_i) &= V_{ik}'(\lambda_i) - \beta \sum_{l=1}^v \frac{N_l}{v} \left\{ \int_0^{\omega_{il}'} K_{il} W_k^l(1) dv_l + \lambda_i \int_{\omega_{il}, \omega_{kl}} V_{il} W_k^l(1) dv_l \right\} \\
 V_{ik}'(\lambda_i) &= \lambda_i V_{ik} + \sum_{l=1}^v \frac{N_l}{v} \left\{ \lambda_i \int_0^{\omega_{kl}'} V_{il} dv_l - \int_0^{\omega_{kl}} K_{il} dv_l \right\} \quad (8) \\
 K_{il}(\lambda_l) &= \int_0^{\lambda_i} V_{il} e^{-\beta W_i^l(\lambda_i)} d\lambda_i; \quad l \text{ in } \omega_{il}
 \end{aligned}$$

where ω_{il}' and ω_{kl}' are the non-overlapping parts of the regions of repulsion for l around i and k , and ω_{kl} is the overlapping part of these regions. Solution of these equations for several types of intermolecular forces has been undertaken. The case of electrolytes will be discussed in a later section of this article. Fortunately we do not need to know K_{il} in this case. Solution has also been attempted for a system of spherical molecules with short-range attractive forces. In this case K_{il} must be known and has been estimated with some success for pure liquids. This work will be reported in a later article.

For the calculation of the integrals G_{ik} and J_{ik} appearing in equation 4, it is necessary to know the potential $W_i^k(\lambda_i)$ both inside and outside the sphere of exclusion ω_{ik} . While considerable progress has been made in the calculation of the G_{ik} , direct attempts to evaluate the J_{ik} have not yet been successful. Inside ω_{ik} , $W_i^k(\lambda_i)$ is of course positive and very large except when λ_i is near zero, so that the integrand $V_{ik} e^{-\beta W_i^k(\lambda_i)}$ has a sharp peak near $\lambda_i = 0$ and vanishes elsewhere. A crude approximation, not valid at liquid densities, is obtained by setting $W_i^k(\lambda_i)$ equal to $\lambda_i V_{ik}$, yielding $J_{ik} = kT \omega_{ik}$. Indirect methods of approach have yielded fair approximations to J_{ik} in pure liquids, but in mixtures the problem has not been solved, except under certain arbitrary assumptions about the entropy of solvation.

We return to equation 4 for the chemical potential, which we write in the following form

$$\begin{aligned}
 \mu_i &= kT \log x_i + \sum_{k=1}^v \frac{N_k}{v} G_{ik} + \mu_i^* \\
 \mu_i^* &= kT \log \bar{v} + \sum_{k=1}^v \frac{N_k}{v} J_{ik} + \varphi_i(T) \quad (9)
 \end{aligned}$$

where \bar{v} is the mean molal volume of the solution, and x_1, \dots, x_2 are the mole fractions of the several components. Let us now suppose that our solution contains N_i' molecules which are of the same shape and volume as molecules of type i but which exert no attractive forces on their neighbors. Although such molecules may have arbitrary shape, we shall find

it convenient to refer to them as hard spheres. For a hard sphere all G_{ik} are zero. Referring again to equation 4, we find for the chemical potential of a hard sphere

$$\mu_i' = kT \log x_i' - kT \log \bar{v}' + \sum_{k=1}^{i+1} \frac{N_k}{v} J_{ik} + \varphi_i(T) \quad (10)$$

where x_i' is the mole fraction of the hard spheres and \bar{v}' is the mean molal volume of the solution augmented by N_i' hard spheres, the summation over all components of course including them. We now observe that the limit of

$$\mu_i' - kT \log x_i'$$

as $x_i' \rightarrow 0$ is simply μ_i^* of equation 9. Thus μ_i^* is the non-ideal part of the chemical potential of hard spheres of type i at infinite dilution in a solvent consisting of the solution under investigation.²

For thermodynamic purposes, it is convenient to choose some reference value of the chemical potential, μ_i^0 , and to define an activity coefficient which measures the departure of $\mu_i - \mu_i^0$ from its ideal value $kT \log x_i$. When the mole fraction of the component is large, or when solutions are to be studied in which its mole fraction varies over a wide range, it is customary to choose μ_i^0 as the chemical potential of the pure liquid component at the same temperature and pressure as the solution,

$$\mu_i = kT \log f_i x_i + \mu_i^0 \quad (11)$$

where the activity coefficient f_i approaches unity as the mole fraction x_i tends to unity. On the other hand, if one component, the solvent, is present in large excess at all compositions of interest, it is convenient to choose the reference value, μ_i^0 , for a solute component as the limit of $\mu_i - kT \log x_i$ as the mole fraction of the solvent, x_s , approaches unity.

$$\mu_i = kT \log \gamma_i x_i + \mu_i^0 \quad (12)$$

$$\mu_i^0 = \lim_{x_s \rightarrow 1} \mu_i - kT \log x_i$$

where γ_i is an activity coefficient which approaches unity as the solution becomes infinitely dilute with respect to all solute species. It is often convenient to use the molarity or the concentration of species i in place of its mole fraction. In dilute solution these variables are nearly proportional

² The formal and thermodynamic aspects of the separation of the chemical potential into parts arising from different types of intermolecular force are discussed by Bell and Gatty (Phil. Mag. **19**, 66 (1935)). Our hard sphere species corresponds to the solute with "limited interaction" of Bell and Gatty.

to one another and the corresponding activity coefficients are nearly equal. From equation 9, we obtain for the first choice of μ_i^0 , the chemical potential of pure liquid i ,

$$\mu_i^0 = NG_{i,i}^0/\bar{v}_i^0 + \mu_i^{*0}$$

where $G_{i,i}^0$ is to be calculated with a distribution function $e^{-\beta w_i^A(\lambda)}$ appropriate to the pure liquid component and μ_i^* is the non-ideal part of the chemical potential of a hard sphere of the same size as molecules of type i , at infinite dilution in pure i . By subtraction and use of the relation

$$1/\bar{v}_i = N_i/v + \sum_{k \neq i} N_k \bar{v}_k/v\bar{v}_i$$

we obtain

$$kT \log f_i/f_i^* = \sum_{k=1}^r \frac{N_k}{v} \left(G_{ik} - \frac{\bar{v}_k}{\bar{v}_i} G_{ii} \right) + \frac{NG_{ii}}{\bar{v}_i} - \frac{NG_{i,i}^0}{\bar{v}_i^0} \quad (13)$$

$$kT \log f_i^* = \mu_i^* - \mu_i^{*0}$$

If the μ_i^0 is chosen at infinite dilution in a solvent s , we have

$$\mu_i^0 = NG_{i,s}^0/\bar{v}_s^0 + \mu_i^{*(s)} \quad (14)$$

where $\mu_i^{*(s)}$ is the chemical potential of a hard sphere of type i at infinite dilution in the pure solvent. We then obtain for the activity coefficient γ_i the following expression.

$$kT \log \frac{\gamma_i}{\gamma_i^*} = \sum_{\substack{k=1 \\ k \neq s}}^r \frac{N_k}{v} \left(G_{ik} - \frac{\bar{v}_k}{\bar{v}_i} G_{ii} \right) + \frac{NG_{ii}}{\bar{v}_i} - \frac{NG_{i,i}^0}{\bar{v}_i^0} \quad (15)$$

$$kT \log \gamma_i^* = \mu_i^* - \mu_i^{*(s)}$$

For exact calculations, we must be able to say something about the chemical potential μ_i^* of the hard spheres. Since direct calculations of the J_{ik} have not yet been successful, only provisional statements about μ_i^* may be made. At this point it is of interest to mention an empirical means of estimating $\mu_i^* - \mu_i^{*(s)}$ similar to a method due to Scatchard (18), who recognized the need for such a correction in the case of electrolytes. He proposed to use the solubilities of the noble gases for this purpose. The noble gases approximate hard spheres, at least in polar solvents, since their attractive forces are weak relative to those between polar molecules. In the present formulation γ_i^* would be equal to the limit of p^*/p_0^* as the pressure of the noble gas tends to zero, where p^* and p_0^* are the gas fugacities in equilibrium with equal mole fractions of the dissolved gas in

the actual solution and in the pure solvent. This limit is equal to K/K_0 , the ratio of the Henry's law constants of the gas for the solution and for the pure solvent. By a process of size interpolation among the several noble gases, it should be possible to pick a value appropriate to the size of a given solute molecule. Given the data, this would at least provide a means of estimating errors introduced by the customary neglect of the term $\mu_i^* - \mu_i^{*(s)}$ in theories of dilute solutions.³

There is another method of estimating μ_i^* , based upon certain assumptions about the entropy of solvation of a hard sphere. From thermodynamics we know that μ_i is equal to $\bar{H}_i - T\bar{S}_i$, or to an adequate approximation in condensed system, $\bar{E}_i - T\bar{S}_i$, where \bar{H}_i , \bar{E}_i , and \bar{S}_i are the partial molal heat content, energy, and entropy of component i . Now the energy of a solution is easily calculated as

$$E = \frac{1}{2} \sum_{k,l} \frac{N_k N_l}{v} B_{kl} + \sum_{k=1}^N N_k E_k^0(T) \quad (16)$$

$$B_{kl} = \int_{\omega_{kl}} V_{kl} e^{-\beta W_{kl}^i(1)} dv_l$$

where $E_k^0(T)$ is the sum of the internal energy and the average rotational and translational kinetic energy of a molecule of type k , depending only on the temperature. The B_{ik} are calculated with the distribution function $W_i^k(1)$, which always makes $e^{-\beta W_i^k(1)}$ vanish in the region of repulsion ω_{ik} , so that no contribution to the integral arises from this region. The B_{ik} all vanish for a hard sphere. If we imagine hard spheres of type i to be present, they can influence the energy of the solution only by their effect on the volume and on the relative distribution of the other molecules. Neglecting the latter effect, and calculating \bar{E}_i^* for a hard sphere of type i , we obtain

$$\bar{E}_i^* = \left(\frac{\partial E}{\partial N_i} \right)_{T, p, N_k \dots} = -\frac{\bar{v}_i^*}{2v^2} \sum_{k,l} N_k N_l B_{kl} + E_i^0(T) \quad (17)$$

where, since \bar{E}_i^* is to be taken at infinite dilution with respect to the hard spheres, the B_{kl} and v are those of the actual solution. The partial molal volume \bar{v}_i^* of the hard spheres is not necessarily equal to \bar{v}_i , that of the actual species i , but in many cases the two will be very nearly equal. We now tentatively assume that \bar{S}_i^* is the same for all solutions and pure liquids at the same temperature and pressure, remembering that \bar{S}_i^* is the

³ A similar method was first proposed by Bjerrum and his coworkers (Trans. Faraday Soc. **23**, 445 (1927); Z. physik. Chem. **127A**, 358 (1927); **159**, 194 (1932)).

non-ideal part of the partial molal entropy of the hard spheres at infinite dilution in the given solution. This assumption cannot as yet be justified by exact reasoning, and it probably is not valid or only approximately valid when one has to do with components of unequal molecular size. When applied to solutions whose components are identical in molecular size and shape, the assumption is entirely reasonable, for since the hard sphere exerts no attractive forces on the other molecules of the solution, its motion in the system is determined solely by the repulsive forces exerted on it by the other molecules, in other words by their size, shape, and packing. Under this assumption the chemical potential of a hard sphere depends upon the solution in which it is immersed only through \bar{E}_i^* . This term arises from the pushing of the other molecules of the solution apart, an effect which may be likened to that of the introduction of a microscopic bubble into the solution. The corresponding values of f_i^* and γ_i^* are the following

$$\begin{aligned} kT \log f_i^* &= -\frac{\bar{v}_i^*}{2} \left[\sum_{k,l}^r \frac{N_k N_l}{v^2} B_{kl} - \frac{N^2 B_{ii}^0}{\bar{v}_i^{02}} \right] \\ k \log \gamma_i^* &= -\frac{\bar{v}_i^*}{2} \left[\sum_{k,l}^r \frac{N_k N_l}{v^2} B_{kl} - \frac{N^2 B_{ii}^0}{\bar{v}_i^2} \right] \end{aligned} \quad (18)$$

where \bar{v}_i^* is assumed to have the same value in the solution and in the reference liquid, in the first case pure liquid i , and in the second pure solvent. For future reference, we shall express $kT \log \gamma_i^*$ in a form suitable for dilute solutions in which only solute concentrations appear.

$$\begin{aligned} kT \log \gamma_i^* &= -\frac{\bar{v}_i^*}{\bar{v}_s^2} \sum_{k=1}^r \frac{v_k}{v} [\bar{v}_s B_{is} - \bar{v}_k B_{ss}] \\ &\quad - \frac{\bar{v}_i^*}{2\bar{v}_s^2} \sum_{k,l}^r \frac{N_k N_l}{v^2} [\bar{v}_s^2 B_{kl} + \bar{v}_l^2 B_{ss} - 2\bar{v}_s \bar{v}_l B_{ks}] \end{aligned} \quad (19)$$

where all molal volumes are assumed independent of composition.

Scatchard (17) and Hildebrand and Wood (8, 9) have proposed an equation for non-electrolyte mixtures, based upon two primary assumptions: (a) the entropy of mixing is ideal; (b) the probability distribution is the same for all molecular pairs in the solution and is independent of composition. In our notation the Scatchard-Hildebrand equation may be written

$$kT \log f_i = \frac{\bar{v}_i}{2} \sum_{k,l}^r \frac{N_k N_l \bar{v}_k \bar{v}_l}{v^2} \left[\frac{2B_{ik}}{\bar{v}_i \bar{v}_k} - \frac{B_{kl}^0}{\bar{v}_k \bar{v}_l} - \frac{B_{ii}^0}{\bar{v}_i^2} \right] \quad (20)$$

where the partial molal volumes are assumed independent of composition and the B_{ki}^0 are computed with a distribution function appropriate to any one of the pure liquid components. It is interesting to note the conditions under which our equations 13 and 18 reduce to the Scatchard-Hildebrand equation. This occurs when all $W_i^k(\lambda_i)$ are independent not only of composition, but also of λ_i . When the $W_i^k(\lambda_i)$ are independent of composition the term

$$G_{ii}/\bar{v}_i - G/i_i\bar{v}_i^0$$

vanishes. When they are independent of λ_i , the G_{ik} reduce to the corresponding B_{ik} . If, in addition, we suppose that the partial molal volume \bar{v}_i^* is equal to \bar{v}_i , and that all \bar{v}_k are independent of composition, our equations 9 and 18 reduce to equation 20 after some algebraic transformations involving the relation

$$1/\bar{v}_i = \left(N_i + \sum_{k \neq i}^v N_k \bar{v}_k / \bar{v}_i \right) / v$$

An investigation of the $W_i^k(\lambda_i)$ in liquids consisting of spherical molecules with short-range attractive forces, now in progress, has shown that when the attractive forces between different components do not differ greatly, the function $W_i^k(\lambda_i)$ is determined primarily by molecular size. This conclusion is not especially remarkable, and has been reached by others on qualitative grounds. However, when this is true, we find that $W_i^k(\lambda_i)$ is practically independent of λ_i except when λ_i is nearly zero, which requires the G_{ik} to reduce effectively to the B_{ik} . When all components of the solution are of the same molecular size, $W_i^k(\lambda_i)$ also becomes independent of composition, and the two major conditions for the validity of the Scatchard-Hildebrand equation are fulfilled.

Guggenheim (6) has developed an interesting theory of solutions, which makes no attempt to go into the fine points of molecular distribution. His theory bears a marked resemblance to lattice theories of the solid state, as does a somewhat earlier theory of Heitler (7). Guggenheim confirms the Scatchard-Hildebrand equation for equal molecular sizes and random distribution of pairs of the type previously discussed. He also proposes an approximate method for taking departures from random distribution into account when the attractive forces between like and unlike pairs are considerably different. Guggenheim's approach is quite different from ours and in many ways simpler. However, while it is probably adequate to deal with problems concerning the energy of mixing and solution, it fails to take account of the non-ideal entropy of mixing in a formally satisfactory manner. We shall present briefly an extension of

the Guggenheim theory, which takes formal account of the entropy of mixing, a step which is necessary in estimating its possibilities.

Guggenheim assumes that as in crystals V_N , the potential of intermolecular forces, has a number of sharp minima of equal depth in the configuration space of the system of N molecules. In perfect crystals, there are just $\prod_{s=1}^r N_s!$ of these minima, one for each permutation of molecules of the same species, which just cancels out this factor in the denominator of the right-hand side of equation 1. On the other hand, in some liquid mixtures, where attractive forces between like and unlike molecules are not very different from those between like molecules, the minima in V_N occur for permutations of unlike molecules as well so that they are $(\sum_{s=1}^r N_s)!$ in number. The phase integral of equation 1 is then equal to $(\sum_{s=1}^r N_s)! I_N$, where I_N is the value of Z_N taken over the region in the neighborhood of one of the minima. From equation 1 we then obtain for the free energy of the solution

$$F_N = + \sum_{k=1}^r N_k kT \log x_k - kT \log I_N + \sum_{k=1}^r N_k \varphi_k(T) \quad (21)$$

where factorials have been approximated by Sterling's formula. Guggenheim then approximates I_N by $e^{-\beta \bar{V}_N} v^N$ where \bar{V}_N is its value at the minimum (also the average potential energy in this theory), and v is a proper volume in which a molecule is free to move. For the theory to be of value, the dependence of this quantity v on composition must be investigated. Guggenheim applies his theory only to cases in which it is reasonable to assume v independent of composition. However, it is possible to get a deeper insight into this question in the following manner. In order to evaluate I_N by peak integration, it is necessary to expand V_N in a Taylor's series in normal coordinates $q_1 \cdots q_{3N}$ specifying the displacement of the system of N molecules from the point in configuration space corresponding to the minimum value of V_N and the maximum of $e^{-\beta V_N}$,

$$V_N = \bar{V}_N + \frac{1}{2} \sum_{s=1}^{3N} \left(\frac{\partial^2 V_N}{\partial q_s^2} \right)_0 q_s^2 + \cdots \quad (22)$$

where the linear terms in the q_k do not appear, since all first derivatives of V_N vanish at the minimum, and, by the use of normal coordinates, all cross derivatives $(\partial^2 V_N / \partial q_s \partial q_k)_0$ are made to vanish. The derivative $(\partial^2 V_N / \partial q_s^2)_0$ are equal to $2\pi^2 M_s \nu_s^2$, where M_s is a function of the masses of the N molecules, and the ν_s is one of the normal frequencies, in terms of

which the vibration of the system around the position of minimum V_N is described, in other words one of the Debye frequencies of the solution. In the peak integration, the q_s are followed to range between $-\infty$ and $+\infty$ with the result

$$I_N = e^{-\beta \bar{V}_N} \left[\prod_{s=1}^{3N} \frac{1}{\nu_s} \right] \prod_{s=1}^{3N} \left(\frac{kT}{2\pi M_s} \right)^{1/2} \quad (23)$$

Substitution of this expression into equation 21 gives

$$F_N = \sum N_k kT \log x_k + \bar{V}_N + \sum kT \log \nu_s + \sum N_k \phi_k(T) \quad (24)$$

where the factors $(kT/2\pi M_s)^{1/2}$ are absorbed into the temperature functions $\phi_k(T)$. Thus Guggenheim's effective volume v is proportional to the mean reciprocal of the Debye frequencies of the solution

$$\log v = \frac{1}{N} \sum_{s=1}^{3N} \log \nu_s^{-1} \quad (25)$$

except for an additive constant dependent only on the temperature. It is no easy task to determine the dependence of the mean Debye frequency on composition, and it should be pointed out that not only molecular size, but also the attractive forces must enter into such a calculation. However, in a nearly ideal solution, where the assumption of approximately equal depths for all minima of V_N is justified, it is reasonable to suppose that v is rather insensitive to changes in composition of the solution. This is not necessarily true in Guggenheim's extension of his theory to take into account the inequalities in the depths of the minima for unequal attractive forces. Moreover, in the latter case the Debye frequencies must be averaged, not only over all normal modes for a single permutation of the molecules, but also over all such permutations. It appears that an exact treatment of the entropy of mixing, into which the v must enter, is even more difficult by the Guggenheim method than by our own.

III. THE RÔLE OF ELECTROSTATIC FORCES

We shall for the present be concerned with moderately dilute solutions. Let us denote γ_i/γ_i^* by γ'_i . It is also convenient to write equation 15 in a slightly different form.

$$kT \log \gamma'_i = \sum_{k \neq i} \frac{N_k}{v} G_{ik} + \frac{N_i}{v} G_{ii} - \frac{NG_{i,i}^0}{\bar{v}_i^0} \quad (26)$$

We shall not attempt to calculate the hard sphere contribution γ_i^* , but we should remember that to obtain the true activity coefficient γ'_i must be

multiplied by this quantity. An estimate of γ_i^* in dilute solutions is given by equation 19.

In this section we shall be particularly interested in solutions containing ions and dipoles. While for non-polar solutions the difference between G_{is} and G_{is}^0 may often be ignored, this is not true in solutions containing ions or dipole molecules, for the pair distribution functions $W_i^*(\lambda_i)$ are no longer even approximately independent of composition. Let us consider a solution consisting of a mixed electrolyte furnishing ν ionic species of charges e_k in a solvent consisting of dipole molecules. The potentials of intermolecular force for the different types of molecular pairs are the following,

$$\begin{aligned} V_{ik} &= e_i e_k / r_{ik} \\ V_{is} &= e_i \mathbf{u}_s \cdot \nabla_s \left(\frac{1}{r_{is}} \right) \end{aligned} \quad (27)$$

where r_{ik} is the distance between the ion pair i and k , and r_{is} is the distance between anion i and a solvent molecule of dipole moment \mathbf{u}_s . For $N_s G_{is}/v$, we have from equations 4 and 27

$$\frac{N_s G_{is}}{v} = \int_0^1 \int_{\omega_{is}} \frac{N_s}{v} e_i \mathbf{u}_s \cdot \nabla_s \left(\frac{1}{r_{is}} \right) e^{-\beta W_i^*(\lambda_i)} dv_s d\omega_s \quad (28)$$

where for clearness we indicate the orientation of a solvent molecule explicitly, $d\omega_s$ being a normalized differential element of its orientation space, while dv_s refers only to its translational configuration space. We remark that

$$\frac{N_s e^{-\beta W_i^*(\lambda_i)}}{v}$$

is the average density of solvent molecules having a specified orientation ω_s at a specified distance, r_{is} , from ion i . Thus the integral

$$(N_s/v) \int \mathbf{u}_s e^{-\beta W_i^*(\lambda_i)} d\omega_s$$

is the average density of electric moment or local polarization \mathbf{P} of the solvent in the vicinity of ion i , charged to a fraction λ_i of its full charge e_i , and we may write

$$\frac{N_s G_{is}}{v} = \int_0^1 \int_{\omega_{is}} e_i \mathbf{P} \cdot \nabla_s \left(\frac{1}{r_{is}} \right) dv_s d\lambda_i \quad (29)$$

If ${}^i\mathbf{D}(r_{is})$ is the local dielectric displacement, we may define a local dielectric constant, ${}^i\epsilon$ by the relation

$${}^i\mathbf{P} = \frac{1}{4\pi} \frac{{}^i\epsilon - 1}{{}^i\epsilon} {}^i\mathbf{D} \quad (30)$$

where the local dielectric constant, ${}^i\epsilon$, may of course differ from the macroscopic dielectric constant, ϵ , of the solution and may depend upon ${}^i\mathbf{D}$ if there is electrical saturation. Except for possible terms of dipole symmetry, the local dielectric displacement is equal to the sum of $-\lambda_i e_i \nabla_s (1/r_{is})$ and the mean values of $-e_k \nabla_s (1/r_{ks})$, arising from the other ions k , averaged with i fixed

$${}^i\mathbf{D}(r_{is}) = -\lambda_i e_i \nabla_s \left(\frac{1}{r_{is}} \right) - \sum_{k=1}^{\nu} \frac{N_k}{v} e_k \int_{\omega_{ik}}^v \nabla_s \left(\frac{1}{r_{ks}} \right) e^{-\beta w_i^k(\lambda_i)} dv_k \quad (31)$$

Substitution of equations 30 and 31 in equation 29 yields

$$\begin{aligned} \frac{N_s G_{is}}{v} = & - \int_0^1 \int_{\omega_{ik}}^v \lambda_i \frac{{}^i\epsilon - 1}{4\pi {}^i\epsilon} \frac{e_i^2}{r_{is}^4} dv_s d\lambda_i \\ & - \sum_{k=1}^{\nu} \frac{N_k e_i e_k}{v} \int_0^1 \int_{\omega_{ik}}^v \int_{\omega_{is}}^v \frac{{}^i\epsilon - 1}{4\pi {}^i\epsilon} \nabla_s \left(\frac{1}{r_{is}} \right) \cdot \nabla_s \left(\frac{1}{r_{ks}} \right) e^{-\beta w_i^k(\lambda_i)} dv_s dv_k d\lambda_i \end{aligned} \quad (31a)$$

We remark that if the regions of repulsion ω_{ik} and ω_{is} are small spheres of arbitrary radius, it is easy to carry out the integration over s by means of Green's theorem, which transforms it to a surface integral on the spheres, ω_{is} .

$$\int_{\omega_{is}}^v \nabla_s \left(\frac{1}{r_{is}} \right) \cdot \nabla_s \left(\frac{1}{r_{ks}} \right) = \frac{4\pi}{r_{ik}} \quad (32)$$

Using this relation, we may write

$$\begin{aligned} \frac{N_s G_{is}}{v} = & \sum_{k=1}^{\nu} \frac{N_k}{v} [G_{ik}^{(s)} - G_{ik}] + A_{is} \\ G_{ik} = & \int_0^1 \int_{\omega_{ik}}^v \frac{e_i e_k}{r_{ik}} e^{-\beta w_i^k(\lambda_i)} dv_k d\lambda_i \\ G_{ik}^{(s)} = & \int_0^1 \int_{\omega_{ik}}^v V_{ik}^{(s)} e^{-\beta w_i^k(\lambda_i)} dv_k d\lambda_i \\ V_{ik}^{(s)} = & \frac{e_i e_k}{\epsilon r_{ik}} + \frac{e_i e_k}{4\pi} \int_{\omega_{is}}^v \frac{\epsilon - {}^i\epsilon}{\epsilon {}^i\epsilon} \nabla_s \left(\frac{1}{r_{is}} \right) \cdot \nabla_s \left(\frac{1}{r_{ks}} \right) dv_s \\ A_{is} = & - \frac{e_i^2}{4\pi} \int_0^1 \int_{\omega_{is}}^v \frac{{}^i\epsilon - 1}{{}^i\epsilon} \frac{1}{r_{is}^4} dv_s d\lambda_i \end{aligned} \quad (33)$$

where ϵ is the macroscopic dielectric constant of the solution. If the deviation of the local dielectric constant ϵ from ϵ can be neglected, $V_{ik}^{(s)}$ reduces simply to $e_i e_k / \epsilon r_{ik}$, the electrostatic energy of a pair of charges in a uniform dielectric continuum. As the distance r_{ik} increases, ϵ must approach ϵ . Near ion i , it may be expected to deviate from ϵ , owing to electrical saturation and to variations of the local density of the solvent from its average density. To investigate this effect from a molecular point of view, it is necessary to study the potential of average force and torque on a solvent dipole in the vicinity of an ion. Without detailed calculation, it is easy to see that the deviation of $V_{ik}^{(s)}$ from $e_i e_k / \epsilon r_{ik}$ will have only the effect of imposing a short-range force upon the Coulomb force, for since $\epsilon - \epsilon$ approaches zero at large values of r_{ik} , the integral certainly decreases more rapidly than $1/r_{ik}$.

For an ionic constituent of an electrolyte solution in a polar solvent we may therefore write

$$kT \log \gamma_i' = \sum_{k=1}^v \frac{N_k}{v} G_{ik}^{(s)} + A_{is} - A_{is}^0 \quad (34)$$

$$A_{is} - A_{is}^0 = \frac{e_i^2}{4\pi} \int_0^1 \int_{\omega_{is}}^v \left[\frac{1}{\epsilon} - \frac{1}{\epsilon_0} \right] \frac{1}{r_{is}^3} dv_s d\lambda_i$$

where ϵ_0 is the local dielectric constant of the pure solvent near an ion i at infinite dilution. We have assumed that the polarization of the solution was due entirely to the permanent dipole moments of the solvent molecules, and have ignored the small contribution due to induced polarization of the solvent and the solute. This may be taken into account by introducing terms of the form V_{iks} into V_s , where V_{iks} is of the form $\alpha_s \nabla_s (1/r_{is}) \cdot \nabla_s (1/r_{ks})$, α_s being the polarizability of a solvent molecule. By an analysis similar to the preceding one, equation 34 is again obtained, the local dielectric constant ϵ including the effect of induced polarization. It should also be mentioned that short-range van der Waals forces between the ions can be included by adding their potential to $V_{ik}^{(s)}$. It is possible to take account of the influence of the solvent on the potential of average force $W_i^k(\lambda_i)$, through the potential $V_{ik}^{(s)}$. We may write equation 6 for a pair of solute molecules in the following form.

$$W_i^k(\lambda_i) = \lambda_i V_{ik} + \sum_{l=1}^v \frac{N_l}{v} \int_0^{\lambda_i} \int_0^v V_{il} \left(e^{-\beta W_i^l(\lambda_i)} - e^{-\beta W_i^l(\lambda_i)} \right) dv_l d\lambda_i \quad (35)$$

$$+ \frac{N_s}{v} \int_0^{\lambda_i} \int_0^v V_{is} \left(e^{-\beta W_{is}^s(\lambda_i)} - e^{-\beta W_{is}^s(\lambda_i)} \right) dv_s d\omega_s d\lambda_i$$

The last integral

$$(N_s/v) \int^{\lambda_i} \int_0^v V_{is} e^{-\beta w_i^{(s)}(\lambda_i)} dv_s d\lambda_i$$

is equal to $N_s G_{is}/v$ and is given by equation 33. To obtain the first integral we proceed in a similar manner

$$\frac{N_s}{v} \int^{o_s} V_{is} e^{-\beta w_{ik}^{(s)}(\lambda_i)} d\lambda_s = e_i {}^{ik}\mathbf{P} \cdot \nabla_s \left(\frac{1}{r_{is}} \right) \quad (36)$$

where ${}^{ik}\mathbf{P}$ is the average local polarization of the solvent near the fixed ion pair i and k . There will be a corresponding local dielectric constant ${}^{ik}\epsilon$, and the dielectric displacement is

$${}^{ik}\mathbf{D} = -\lambda_i e_i \nabla_s \left(\frac{1}{r_{is}} \right) - e_k \nabla_s \left(\frac{1}{r_{ks}} \right) - \sum_{l=1}^r \frac{N_l}{v} \int^v e_l \nabla_s \left(\frac{1}{r_{sl}} \right) e^{-\beta w_{lk}^{(l)}(\lambda_i)} dv_l \quad (37)$$

Substitution of $[({}^{ik}\epsilon - 1)/4\pi {}^{ik}\epsilon] {}^{ik}\mathbf{D}$ for ${}^{ik}\mathbf{P}$ in equation 36 and integration over s leads to an expression similar to equation 33, with some additional terms. Finally one obtains equation 35 in the following form

$$\begin{aligned} W_i^k(\lambda_i) &= \lambda_i V_{ik}^{(s)}({}^{ik}\epsilon) + A_{is}({}^{ik}\epsilon) - A_{is}({}^i\epsilon) \\ &+ \sum_{l=1}^r \frac{N_l}{v} \int_0^{\lambda_i} \int [V_{il}^{(s)}({}^{ik}\epsilon) e^{-\beta w_{lk}^{(l)}(\lambda_i)} - V_{il}^{(s)}({}^i\epsilon) e^{-\beta w_{lk}^{(l)}(\lambda_i)}] dv_l d\lambda_i \end{aligned} \quad (38)$$

where $V_{ik}^{(s)}$ and A_{is} are again given by equation 33, the notation $V_{ik}^{(s)}({}^{ik}\epsilon)$ meaning that the local dielectric constant ${}^{ik}\epsilon$ appears instead of ${}^i\epsilon$. Finally, if the deviations of the local dielectric constants from the macroscopic dielectric constant can be neglected, the equation takes the form

$$\begin{aligned} W_i^k(\lambda_i) &= \lambda_i V_{ik}^{(s)} + \sum_{l=1}^r \frac{N_l}{v} \int_0^{\lambda_i} \int_0^v V_{il}^{(s)} [e^{-\beta w_{lk}^{(l)}(\lambda_i)} - e^{-\beta w_{lk}^{(l)}(\lambda_i)}] dv_l d\lambda_i \\ V_{ik}^{(s)} &= V_{ik}/\epsilon \end{aligned} \quad (39)$$

the equation for the potential of average force between a pair of ions, in which the solvent plays the rôle of a dielectric continuum, the sole effect of which is to multiply the V_{ik} by a factor $1/\epsilon$. We shall presently undertake the solution of equation 39 with certain approximations.

Not only when the solute molecules are ions, but whenever the attractive forces between them are principally electrostatic in nature, equations 39 and 34 may be used for the calculation of the potential of average force and the activity coefficients, the $G_{ik}^{(s)}$ being given by

$$G_{ik}^{(s)} = \int_0^1 \int_0^v V_{ik}^{(s)} e^{-\beta w_{ik}^{(s)}(\lambda_i)} dv_k d\lambda_i \quad (40)$$

If the local dielectric constants are approximated by the macroscopic dielectric constant, $V_{ik}^{(s)}$ is reduced to V_{ik}/ϵ . Electrostatic forces between solute molecules are generally of predominant importance only for electrolytes and polar molecules. The three most important types of interaction are therefore those between two ions, between an ion and a dipole, and between dipoles. The first has already been considered. The other two types of forces have potential $V_{ik}^{(s)}$ of the form

$$\begin{aligned} V_{ik}^{(s)} &= \frac{e_i}{\epsilon} \mu_k \cdot \nabla_k \left(\frac{1}{r_{ik}} \right); \text{ ion-dipole} \\ V_{ik}^{(s)} &= \frac{1}{\epsilon} (\mu_i \cdot \nabla_i) (\mu_k \cdot \nabla_k) \left(\frac{1}{r_{ik}} \right); \text{ dipole-dipole} \end{aligned} \quad (41)$$

It should be remembered, however, that it is a much poorer approximation to neglect the deviation of the local dielectric constant from the macroscopic one, in the case of ion-dipole and dipole-dipole interaction than in the case of ion-ion interaction, since the former are themselves short-range forces. Also, the effect of the discontinuity of the dielectric constant at the surface of the dipole molecule has been neglected in the above expressions (41), the dipole having been supposed to consist of a pair of charges encased in non-overlapping small spheres, since otherwise the dielectric displacement \mathbf{D} of equation 31 cannot be expressed simply as a sum of Coulomb terms arising from the individual charges of the molecules, but there will be contributions arising from the effect of the cavity made by the molecule in the statistical continuum of the solvent. The effect of the cavity can be calculated easily only if the local dielectric constant is assumed to be ϵ , and the boundary conditions of electrostatics are applied at the surface of the molecule. (Continuity of the potential, the tangential component of the electric field, and the normal component of the dielectric displacement.) For dipole molecules of spherical shape, this leads to corrected expressions for $V_{ik}^{(s)}$.

$$\begin{aligned} V_{ik}^{(s)} &= \left[\frac{3\epsilon}{2\epsilon + 1} \right] \frac{e_i}{\epsilon} \mu_k \cdot \nabla_k \left(\frac{1}{r_{ik}} \right); \text{ ion-dipole} \\ V_{ik}^{(s)} &= \left[\frac{3\epsilon}{2\epsilon + 1} \right]^2 \frac{1}{\epsilon} (\mu_i \cdot \nabla_i) (\mu_k \cdot \nabla_k) \left(\frac{1}{r_{ik}} \right); \text{ dipole-dipole} \end{aligned}$$

The method also leads to an expression for the polarization energy of solvent by a dipole molecule. If the molecule is a sphere, we obtain

$$A_{ss} = \frac{\mu_s^2}{a^3} \frac{1 - \epsilon}{2\epsilon + 1} \quad (43)$$

The potentials of ion-dipole and dipole-dipole interaction are those of short-range forces. For this reason $W_i^k(\lambda_i)$ of equation 39 may be approximated by $\lambda_i V_{ik}^{(s)}$ for an ion-dipole or a dipole-dipole pair. With this approximation, the integrals $G_{ik}^{(s)}$ take the form

$$G_{ik}^{(s)} = kT \int_{\omega_{ik}}^r (1 - e^{-\beta V_{ik}^{(s)}}) dv_k \quad (44)$$

a form reminiscent of the second virial coefficient of gases. If the salting-out term $A_{is} - A_{is}^0$, depending upon the influence of the solute on the dielectric constant of the solution is ignored, the following limiting law for the activity coefficient of a dipole molecule i in a dilute solution, is obtained

$$\log \gamma_i' = \sum_{k=1}^r \frac{N_k}{v} \int_{\omega_{ik}}^v (1 - e^{-\beta V_{ik}^{(s)}}) dv_k \quad (45)$$

where the sum extends over all solute components of the solution, which may include both ions and dipoles. It should be pointed out that this is not a true limiting law for the salting-out term $A_{is} - A_{is}^0$ and the hard sphere factor γ_i^* (equation 19) both contain terms proportional to the solute concentrations N_k/v . Only when these additional terms are small, can equation 45 be a good approximation. This probably is only true for large dipoles such as zwitterions, the electric moments of which are very large in comparison with those of the solute molecules, or perhaps for smaller dipoles when the solvent is non-polar. Equation 45 was first proposed by Fuoss (4) for solutions containing only dipole solutes. His argument was based upon the van't Hoff analogy between the osmotic pressure of a solution and the pressure which the solute would exert as a gas in the same volume. Fuoss' calculation of the osmotic pressure therefore closely parallels the Keesom theory of the equation of state of dipole gases. Fuoss has given asymptotic expressions for the integral

$$\int_{\omega_{ii}}^r (1 - e^{-\beta V_{ii}^{(s)}}) dv_k$$

for elongated elliptical molecules, and has tabulated it for spherical dipole molecules as a function of the parameter $\mu^2/\epsilon a^3 kT$, where μ is the dipole moment and a is the molecular diameter.

One of the most interesting applications of equation 45 is found in the study of the influence of electrolytes upon the activity coefficients of the aliphatic amino acids. It is well established that these acids exist in zwitterionic form in solvents of high dielectric constant. Zwitterions differ from true ions in that they possess no resultant charge, but they are characterized by dipole moments of great magnitude, of the order of 15.0×10^{-18} e.s.u. for α -amino acids. Calculation of $\log \gamma_i$ for spherical

zwitterions with the use of equations 42 and 45 leads to a limiting law in agreement with that obtained by the author (13) on the basis of the Debye-Hückel theory. The calculations have been extended to non-spherical zwitterions, account being taken of the finite separation of the charged groups. The resulting formulas have been applied with success to experimental results of Cohn (2) and his coworkers on the influence of salts upon the solubilities of the amino acids and their peptides. This work will be reported in detail at a later time.

It is of interest to remark that a better approximation to the salting-out term $A_{ii} - A_{ii}^0$, which represents the difference between the energy of polarization in the given solution and in the pure solvent, can be obtained by incorporating a term to take care of it in $V_{ik}^{(s)}$. This may be done by taking the sizes of both molecules i and k into account in the calculation of their electrostatic energy $V_{ik}^{(s)}$ in a medium of dielectric constant ϵ . If the molecules are spherical in shape and a_{is} and a_{ks} are the radii of the respective cavities which they form in the solvent, one obtains for ions the following expression for $V_{ik}^{(s)}$, by applying the boundary conditions of electrostatics

$$V_{ik}^{(s)} = \frac{e_i e_k}{\epsilon r_{ik}} - \frac{1}{2} \frac{e_i^2 a_{is}^3 + e_k^2 a_{ks}^3}{2\epsilon + 1} \frac{\epsilon - 1}{\epsilon} \frac{1}{r_{ik}^4} \quad (46)$$

Similar, but more complicated, expressions may be obtained for ion-dipole and dipole-dipole pairs. If these $V_{ik}^{(s)}$ are used in equation 34, salting out is automatically taken care of and the term $A_{ii} - A_{ii}^0$, a cruder estimate of the effect, does not appear.

IV. STRONG ELECTROLYTES

The potential of mean force $W_i^k(\lambda_i)$ between a pair of ions cannot be approximated by $\lambda_i V_{ik}^{(s)}$, because the long-range character of the interionic forces causes the

$$\int_{\omega_{ik}}^{\infty} (1 - e^{-\beta V_{ik}^{(s)}}) dv_k$$

to diverge. We therefore turn to equation 39 for a better approximation. Equation 39 differs from equation 4 only by the substitution of $V_{ik}^{(s)}$ and $V_{ii}^{(s)}$ for V_{ik} and V_{ii} . By the same set of approximations,

$$W_{ik}^k(\lambda_i) = W_i^l(\lambda_i) + W_k^l(1)$$

and expansion of the exponentials, equation 39 may be transformed into a linear equation like equation 7. Introducing $e_i e_l / \epsilon r_{il}$ for the $V_{il}^{(s)}$, we obtain for ions of equal size

$$W_i^k(\lambda_i) = \lambda_i \frac{e_i e_k}{\epsilon r_{ik}} - \frac{\lambda_i}{kT} \sum_{l=1}^r \frac{N_l}{v} e_l e_i \int_{\omega_{ik}, \omega_{il}}^v \frac{W_k^l(1)}{r_{il}} dv_l \quad (47)$$

where the integrals over the regions of repulsion are omitted for brevity. For ions of equal size, they vanish because of electrical neutrality

$$\sum_{i=1}^r N_i e_i = 0$$

when the solutions $W_i^k(\lambda_i)$ have the form

$$W_i^k(\lambda_i) = \lambda_i \frac{e_i e_k}{\epsilon} g(r_{ik}) \quad (48)$$

where $g(r_{ik})$ is the same function for all ionic species. A more general solution of equation 7 may be obtained by adding to equation 48 a term independent of the ionic charges, $W_i^{k^0}(\lambda_i)$ satisfying the equation

$$\begin{aligned} W_i^{k^0}(\lambda_i) &= u(r_{ik}) - \sum_{l=1}^r \frac{N_l}{v} \int_0^{\omega'_{il}} K_{il} W_l^{k^0}(1) dv_l \\ u(r_{ik}) &= - \sum_{l=1}^r \frac{N_l}{v} \int_0^{\omega_{ikl}} K_{il} dv_l \end{aligned} \quad (49)$$

Thus $W_i^{k^0}(\lambda_i)$ is just the potential of average force between a pair of hard spheres. We shall be interested here only in the part of $W_i^k(\lambda_i)$ dependent upon the ionic charges. It is interesting to remark that a rather tedious analysis shows that the terms neglected in approximating W_{ik}^l by $W_i^l + W_k^l$ are of the same magnitude as the non-linear terms neglected in the expansion of exponentials to obtain equations 47 and 49, so that equations 7, 47, and 49 are exact as linear approximations to equations 4 and 39.

We now introduce the form of equation 48 into equation 47. Since all ions are assumed identical as to size and shape, ω_{ik} and ω_{il} are independent of the ionic species l , as are the integrals

$$\int_{\omega_{ik}, \omega_{il}}^{\infty} [g(r_{kl})/r_{il}] dv_l$$

so that equation 47 becomes

$$\begin{aligned} g(R) &= \frac{1}{R} - \frac{\kappa^2}{4\pi} \int_{\omega_{13}, \omega_{23}}^{\infty} \frac{g(r_{13})}{r_{23}} dv_3 \\ \kappa^2 &= \frac{4\pi}{\epsilon kT} \sum_{l=1}^r \frac{N_l e_l^2}{v} \end{aligned} \quad (50)$$

where R , r_{13} , and r_{23} have been introduced for r_{ik} , r_{kl} , and r_{il} . We remark that κ is identical with the corresponding function in the Debye-Hückel theory. We now assume that the ions are spherical in shape so that ω_{13} and ω_{23} are spherical regions of equal radius a , separated by a distance R ,

which are to be excluded from the region of integration in equation 50. Introducing r_{13} and r_{23} as variables of integration, we have

$$dv_3 = (2\pi/R)r_{13}r_{23}dr_{13}dr_{23}$$

By integration over r_{23} , with proper regard to the influence of ω_{23} upon the limits of integration, we obtain the following integral equation. For simplicity we designate the single remaining variable of integration, r_{13} , by r .

$$\begin{aligned} g(R) &= \varphi(R)/R \\ \varphi(R) &= 1 - \kappa^2 \int_a^\infty K(R, r) \varphi(r) dr \end{aligned} \quad (51)$$

where the kernel $K(R, r)$ has the form

$$\begin{aligned} a \leq R < 2a: K(R, r) &= (r + R - a)/2 & a \leq r < R + a \\ &= R & R + a \leq r < \infty \\ 2a \leq R < \infty: K(R, r) &= r & a \leq r < R - a \\ &= (r + R - a)/2 & R - a \leq r < R + a \\ &= R & R + a \leq r < \infty \end{aligned} \quad (52)$$

If we had neglected the size of one of the ions and extended the integration over ω_{23} , the kernel $K(R, r)$ would have the simpler form

$$\begin{aligned} a \leq R < \infty \\ K(R, r) &= r; a \leq r < R \\ &= R; R \leq r < \infty \end{aligned} \quad (53)$$

With the approximate kernel (53), equation 51 is equivalent to the linear Poisson-Boltzmann equation with boundary conditions, of the Debye-Hückel theory. The unique solution is

$$\varphi(R) = \frac{e^{-\kappa(R-a)}}{1 + \kappa a} \quad (54)$$

a result which may be verified by direct substitution. The corresponding value of $W_i^k(\lambda_i, R)$ is

$$W_i^k(\lambda_i, R) = \frac{\lambda_i e_i e_k}{\epsilon R} \frac{e^{-\kappa(R-a)}}{1 + \kappa a} \quad (55)$$

With the omission of the salting-out term and the hard sphere term, the activity coefficient of a spherical ion of type i may be obtained from equations 40, 33, and 34,

$$kT \log \gamma_i' = \frac{4\pi e_i}{\epsilon} \sum_{k=1}^v \frac{N_k}{v} e_k \int_0^1 \int_a^\infty R(e^{-\beta W_i^k(\lambda_i)} - 1) dR d\lambda_i \quad (56)$$

where, because of electrical neutrality of the solution, the vanishing term $(4\pi e_i/\epsilon) \sum_{k=1}^r (N_k e_k)/v \int_0^1 \int_a^\infty R dR d\lambda_i$ has been subtracted from the left-hand side of equation 56. If $W_i^k(\lambda_i, R)$ has the form 48, and non-linear terms in the expansion of the exponential can be neglected, we have

$$kT \log \gamma'_i = -\frac{e_i^2}{2\epsilon} \kappa^2 \int_a^\infty \varphi(R) dR \quad (57)$$

where $\varphi(R)$ satisfies the integral equation 51. With the solution 54 corresponding to the approximate kernel 53, in which the size of one of the ions is neglected, we obtain the Debye-Hückel (3) result

$$kT \log \gamma'_i = -\frac{e_i^2}{2\epsilon} \frac{\kappa}{1 + \kappa a} \quad (58)$$

The mean activity coefficient of any electrolyte which may be formed from the ions in the solution may be calculated from the individual ion activity coefficients in the usual way.

The solution of equation 51 with the kernel 52, which takes the sizes of both ions of the pair into account, is considerably more difficult. It is found that the solution may be expressed in the form

$$\varphi(R) = \sum_{n=1}^{\infty} A_n e^{-z_n R} \quad (59)$$

where the sum extends over all roots z_n , with positive real parts, of the transcendental equation

$$z^2 - \kappa^2 \cosh za = 0 \quad (60)$$

It is convenient to order the roots according to the magnitudes of their real parts. Several of the denumerably infinite set of roots are tabulated below:

$$z_n = \alpha_n + i\beta_n$$

κa	0.10	1.00	1.03	2.00
$\alpha_1 a$	0.10	1.62	2.07	1.06
$\beta_1 a$	0.00	0.00	0.00	+2.08
$\alpha_2 a$	9.88	2.56	2.07	1.06
$\beta_2 a$	0.00	0.00	0.00	-2.08
$\alpha_3 a$	11.11	6.26		4.84
$\beta_3 a$	± 14.42	± 14.90		± 15.07

When κa is less than 1.03, there are two real roots, one of which remains very nearly equal to κa in dilute solutions. At κa equal to 1.03, the real roots merge into a repeated root, while for greater values of κa , all roots are complex. For small values of κa , all roots except z_1 have very large real parts, so that their contributions to $\varphi(R)$, equal to $e^{-z_n R}$, will decay rapidly as R increases, and so can be important only for small values of R . In more concentrated solutions, $\kappa a > 1.03$, all roots are complex, imparting to $\varphi(R)$ an oscillatory form, characteristic of radial distribution functions in liquids.

By substitution of the form 59 in the integral equation 51 with the kernel 52 for $R > 2a$, it is found that only one condition is imposed upon the coefficient A_n .

$$\sum_{n=1}^{\infty} \frac{A_n}{z_n^2} e^{z_n a} (1 + z_n a) = 1/\kappa^2 \quad (61)$$

However, in order that 59 be a solution in the interval $a \leq R < 2a$, an infinite set of conditions is imposed upon the A_n . Since the $e^{-z_n R}$ doubtless form a complete set of functions, they could be orthogonalized by linear combination in the interval $a \leq R < 2a$, and the properties of orthogonal sets could be used in conjunction with the integral equation for the determination of the A_n . However, this process is rather laborious and cumbersome. A better method, suggested to the writer by Dr. Warschawski

of Cornell University, is to calculate the Laplace transform $\int_0^\infty \varphi(R) e^{-uR} dR$, which is then inverted by means of the Fourier integral theorem. This procedure transforms the integral equation 51 entirely onto the interval $a \leq R < 2a$. Although the resulting integral equation cannot be solved in finite terms, it leads immediately to the desired set of linear relations between the A_n , for a solution of the form 59.

We shall be content here with the construction of an approximate solution, involving only the first two terms of the series 59. Using the two roots z_n with smallest real parts, we can make the solution

$$\varphi(R) = A_1 e^{-z_1(R-a)} + A_2 e^{-z_1(R-a)} \quad (62)$$

fit at the two ends of the interval, $R = a$ and $R = 2a$, and everywhere outside, $R > 2a$. By substitution in equation 51 with the kernel appropriate to $a \leq R < 2a$, the condition that equation 62 be a solution at $R = a$ imposes one linear relation upon the coefficients. A second relation is furnished by equation 61, and we remember that any linear combination of the form 59 is a solution of $R = 2a$ and for all greater values of R . After making some transformations with the aid of equation 60, we have

$$\begin{aligned} A_1(1 + z_1 a)/z_1^2 + A_2(1 + z_2 a)/z_2^2 &= 1/\kappa^2 \\ A_1 e^{z_1 a}/z_1^2 + A_2 e^{z_2 a}/z_2^2 &= 1/\kappa^2 \end{aligned} \quad (63)$$

with solutions

$$\begin{aligned} A_1 &= \frac{z_1^2}{\kappa^2} \frac{e^{-z_1 a} - e^{-(z_1 + z_2)a}(1 + z_2 a)}{(1 + z_1 a)e^{-z_1 a} - (1 + z_2 a)e^{-z_2 a}} \\ A_2 &= \frac{z_2^2}{\kappa^2} \frac{e^{-z_2 a} - e^{-(z_1 + z_2)a}(1 + z_1 a)}{(1 + z_2 a)e^{-z_2 a} - (1 + z_1 a)e^{-z_1 a}} \end{aligned} \quad (64)$$

when $\kappa a < 1.03$, z_1 and z_2 are real, equal to α_1 and α_2 . $W_i^k(\lambda_i, R)$ and $\log \gamma_i'$ may be computed by substitution of equations 62 and 64 into 48 and 57.

$$W_i^k(\lambda_i, R) = \lambda_i \frac{c_i c_k}{\epsilon R} [A_1 e^{-\alpha_1(R-a)} + A_2 e^{-\alpha_2(R-a)}] \quad (65)$$

For the activity coefficient, we obtain

$$kT \log \gamma_i' = -\frac{e_i^2}{2\epsilon} \frac{\alpha_1 e^{-\alpha_1 a}(1 - e^{-\alpha_2 a}) - \alpha_2 e^{-\alpha_2 a}(1 - e^{-\alpha_1 a})}{(1 + \alpha_1 a)e^{-\alpha_1 a} - (1 + \alpha_2 a)e^{-\alpha_2 a}} \quad (66)$$

In dilute solutions, reference to the table of roots shows that $(\alpha_2 a - \alpha_1 a)$ is very large, amounting to about 9.0. Under these circumstances all terms involving $e^{-\alpha_2 a}$ are completely negligible and we have

$$kT \log \gamma_i' = -\frac{e_i^2}{2\epsilon} \frac{\alpha_1}{1 + \alpha_1 a} \quad (67)$$

a result which differs from the Debye-Hückel expression only by the appearance of α_1 instead of κ . But in dilute solutions α_1 differs inappreciably from κ so that the Debye-Hückel result is obtained. When κa is equal to 1.03, the roots z_1 and z_2 merge into a repeated root, and equations 63 have no solutions. However, the expressions 65 and 66 for $W_i^k(\lambda_i, R)$ and the activity coefficient both converge for $\kappa a = 1.03$, although A_1 and A_2 individually diverge. Beyond $\kappa a = 1.03$, the roots z_1 and z_2 become complex conjugates, $\alpha \pm i\beta$ and equations 63 again have solutions. Then $W_i^k(\lambda_i, R)$ takes the form

$$\begin{aligned} W_i^k(\lambda_i, R) &= \lambda_i \frac{c_i c_k}{\epsilon R} e^{-\alpha(R-a)} [A_1 \cos \beta(R-a) + A_2 \sin \beta(R-a)] \\ A_1 &= \frac{1}{\kappa^2} \frac{(\alpha^2 - \beta^2)[\sin \beta a - \beta a e^{-\alpha a}] - 2\alpha\beta[\cos \beta a - (1 + \alpha a)e^{-\alpha a}]}{(1 + \alpha a) \sin \beta a - \beta a \cos \beta a} \\ A_2 &= \frac{1}{\kappa^2} \frac{(\alpha^2 - \beta^2)[\cos \beta a - (1 + \alpha a)e^{-\alpha a}] + 2\alpha\beta[\sin \beta a - \beta a e^{-\alpha a}]}{(1 + \alpha a) \sin \beta a - \beta a \cos \beta a} \end{aligned} \quad (68)$$

For the activity coefficient, we obtain the expression

$$kT \log \gamma'_i = -\frac{e_i^2 \alpha \sin \beta a - \beta (\cos \beta a - e^{-\alpha a})}{2\epsilon (1 + \alpha a) \sin \beta a - \beta a \cos \beta a} \quad (69)$$

In figure 1, equations 66 and 69 are compared with the Debye-Hückel formula (58). In dilute and moderately dilute solutions, $\kappa a < 0.5$, $\log \gamma'_i$ does not differ much from the Debye-Hückel value. However, at higher concentrations, $\kappa a > 1.03$, the deviation becomes appreciable, and $\log \gamma'_i$ fails to approach the Debye-Hückel asymptotic value $-e_i^2/\epsilon a kT$.

The periodic factor in $W_i^*(\lambda_i, R)$, for $\kappa a > 1.03$, is particularly interesting. As κa increases, the real part, α , of z_1 and z_2 diminishes, and the

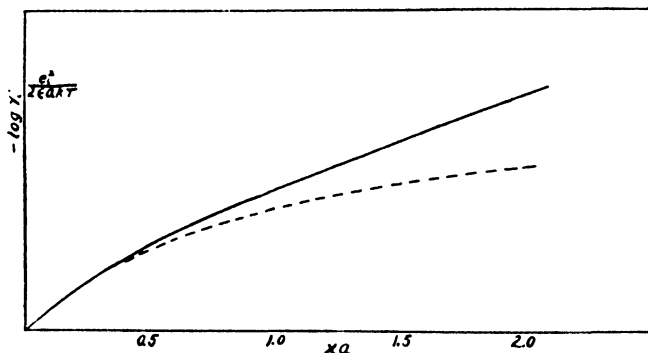


FIG. 1

----- Debye-Hückel equation 58
 ————— Equations 66 and 69.

exponential decay becomes less rapid. In other words the ionic atmosphere expands. At the same time the period of oscillation $2\pi/\beta$, at first very long, tends to a distance slightly exceeding the ionic diameter, a . When κa becomes equal to 2.79, α vanishes and equation 68 is no longer a solution of 51. At higher concentrations, a liquid type of distribution function, if one exists at all, must be constructed from the higher roots of equation 60. For values of κa just less than 2.79, the exponential factor is effectively unity over many molecular diameters, and the corresponding distribution is suggestive of a microcrystalline distribution, with "local" long-range order extending over many molecular diameters. This brings up the intriguing question: Do very concentrated electrolyte solutions ($\kappa a > 2.79$) possess long-range crystalline order in the distribution of the ions, which they contain? A loosely bound statistical lattice might still leave the solution with the elastic properties of a viscous fluid, manifesting

itself chiefly in the optical properties. The answer to this question is probably in the negative, for the solution 68, in which only the first two roots of equation 60 are employed, very likely has only qualitative significance at very high concentrations. The value, $\kappa a = 2.79$, predicted by equation 68 as the limiting concentration for a liquid type of distribution seems altogether too low. Thus in a uni-univalent electrolyte solution with $e_i^2/\epsilon akT$ equal to unity, this value of κa corresponds to a volume about 2.3 times greater than the ions would occupy if packed in a face-centered cubic lattice, with an interionic distance equal to the diameter a .

Better approximations to the solution of equation 51, may be obtained by including terms $e^{-z_n R}$ involving the higher roots of equation 60. The best way to do this is to employ a general method based upon the Laplace transformation. However, the method employed here could be extended by including the terms $e^{-z_n R}$ involving the first m roots (ordered according to the magnitude of their real parts) and determining the coefficients A_n by making the sum $\sum_{n=1}^m A_n e^{-z_n(R-a)}$ a solution of equation 51 at m points on the interval $a \leq R < 2a$. However, even an exact solution of equation 51, although a step in the right direction, could be applied only with caution to very concentrated electrolyte solutions. There is always the question of the error arising from approximating the local dielectric constant by the macroscopic one. This error is doubtless serious when the mole fraction of the electrolyte becomes comparable with that of the solvent. Moreover, even if the macroscopic dielectric constant can be used, it may become so small in very concentrated solutions that it is not permissible to approximate the exponentials in equation 39 by the first two terms of their series expansions. Under these circumstances equation 51 no longer furnishes an adequate approximation to $W_i^k(\lambda_i)$. Another point should be borne in mind. The γ_i' of equation 57 is not the actual activity coefficient, but must be corrected for salting out and multiplied by the hard sphere factor γ_i^* , before comparison with experiment can be made. These latter influences are not negligible in comparison with the pure electrostatic effect, at very high concentrations.

In spite of the fact that equation 51 can be attributed only to qualitative significance in extremely concentrated solutions, it seems reasonable to suppose that it can be used quantitatively in moderately dilute solutions, let us say up to concentrations of 1 mole per liter, as long as $e_i e_k / \epsilon akT$ is small relative to unity for all ion pairs. When this condition is not fulfilled, either equation 39 must be solved without expansion of the exponentials, or a method of the Bjerrum (1) type must be used. Since the error involved in approximating W_{ik}^l by $W_i^l + W_k^l$ is of the same order of magnitude as the non-linear terms in the expansion of the exponentials of equa-

tion 39, the former method is almost hopelessly complicated. The Bjerrum method seems therefore to be the most promising.

V. STATISTICAL MASS ACTION AND THE BJERRUM THEORY OF ION ASSOCIATION

If the potential V_{ik} has a minimum of depth large relative to kT for certain values of the relative coördinates of the molecular pair i and k , and if for this configuration, they exert together only a small attractive force upon neighboring molecules, W_i^k may be approximated by an expression which leads to simple mass action. It is a matter of considerable interest to investigate the nature of this approximation.

Reference to equation 18 of "Statistical Mechanics of Fluid Mixtures" (11) allows us to write the chemical potential of a component i in the form

$$\mu_i = kT \log f_i(1)C_i + \varphi_i(T)$$

$$kT \log f_i(\lambda) = \int_0^\lambda \overline{V_i(t)} dt = \sum_{k=1}^v \frac{N_k}{v} \int_0^\lambda \int_0^v V_{ik} e^{-\beta W_i^k(t,v)} dv_k dt \quad (70)$$

where C_i is the concentration of component i , in any units, conversion factors being absorbed into $\varphi_i(T)$, and $f_i(\lambda)$ is the activity coefficient of a partially coupled molecule i . Let us now consider a potential of average force $W_i^k(\lambda_i, \lambda_k)$, defined for a potential of intermolecular force $V_N(\lambda_i, \lambda_k)$ (equation 7, "Statistical Mechanics of Fluid Mixtures"), in which only the coupling parameters λ_i and λ_k for a single pair of molecules differ from unity.

$$e^{-\beta W_i^k(\lambda_i, \lambda_k)} = \frac{v^2 \int \dots \int e^{-\beta V_N(\lambda_i, \lambda_k)} dv_1 \dots dv_{N-2}}{\int \dots \int e^{-\beta V_N(\lambda_i, \lambda_k)} dv_1 \dots dv_N}$$

$$V_N(\lambda_i, \lambda_k) = V_{N-2} + \lambda_i \lambda_k V_{ik} + \lambda_i V'_i + \lambda_k V'_k \quad (71)$$

$$V'_i = \sum_{\substack{l=1 \\ l \neq k}}^N V_{il} \quad V'_k = \sum_{l=1}^N V_{kl}$$

Equations similar to equation 29 ("Statistical Mechanics of Fluid Mixtures") may be obtained by partial differentiation of equation 71

$$\frac{\partial W_i^k(\lambda_i, \lambda_k)}{\partial \lambda_i} = \lambda_k V_{ik} + \overline{V_i^k(\lambda_i, \lambda_k)} - \overline{V_i'(\lambda_i)}$$

$$\frac{\partial W_i^k(\lambda_i, \lambda_k)}{\partial \lambda} = \lambda_i V_{ik} + \overline{V_k^i(\lambda_i, \lambda_k)} - \overline{V_k'(\lambda_k)} \quad (72)$$

It is unnecessary to indicate the dependence of $\overline{V_i^k(\lambda_i, \lambda_k)}$ on λ_k since, except for a term of zero order, it will be independent of the coupling with

any single molecule of type k . On the other hand ${}^{ik}\overline{V'_i(\lambda_i, \lambda_k)}$, an average with i and k held fixed, will depend on both λ_i and λ_k when the two molecules are in each other's neighborhood. In order to calculate $W_i^k(\lambda, 1)$, we remember that $W_i^k(\lambda_i, \lambda_k)$ must vanish when either λ_i or λ_k is zero. We choose a path of integration in the (λ_i, λ_k) plane consisting of the straight line $\lambda_i = \lambda t$; $\lambda_k = t$ extending from the origin to the point $(\lambda, 1)$. Using this path and the partial derivatives of equation 72, we obtain

$$W_i^k(\lambda, 1) = \lambda V_{ik} + \int_0^1 [\lambda {}^{ik}\overline{V'_i(\lambda t, t)} + {}^{ik}\overline{V'_k(\lambda t, t)}] dt - \int_0^\lambda \overline{V'_i(t)} dt - \int_0^1 \overline{V'_k(t)} dt \quad (73)$$

We note that $\lambda V'_i + V'_k$ is the mutual potential energy of the molecular pair i and k with all the other molecules of the solution. Let us write

$$kT \log f_{ik}(\lambda, 1, q_{ik}) = \int_0^1 [\lambda {}^{ik}\overline{V'_i(\lambda t, t)} + {}^{ik}\overline{V'_k(\lambda t, t)}] dt \quad (74)$$

By reference to equation 70, we see that $f_{ik}(\lambda, 1, q_{ik})$ could be interpreted as an activity coefficient of the compound molecule (ik) , in which the relative coordinates q_{ik} of the pair have some fixed value. This interpretation, while correct is, however, unessential. Referring again to equation 70 and remembering that $\overline{V'_i(t)}$ and $\overline{V'_k(t)}$ can be identified with $\overline{V_i(t)}$ and $\overline{V_k(t)}$ (since in an average in which no molecules are held fixed, any single term $\overline{V_{ik}}$ is of negligible order), we may write equation 73 in the form

$$W_i^k(\lambda, 1) = \lambda V_{ik} + kT \log \frac{f_{ik}(\lambda, 1, q_{ik})}{f_i(\lambda) f_k(1)} \quad (74)$$

The usefulness of this expression is apparent, for if V_{ik} has a deep minimum for some particular configuration q_{ik} , and at the same time f_{ik} is practically unity, $W_i^k(\lambda, 1)$ can be approximated by $\lambda V_{ik} - kT \log f_i(\lambda) f_k(1)$. As will presently be shown, it is this approximation which leads to simple mass action.

From now on, we shall limit our attention to a system of only two components. Using equations 70 and 74, and separating the region of integration for unlike pairs into a region v_0 for small values of their relative coordinates and $v \rightarrow v_0$ for large values, we may write

$$kT \frac{d \log f_1(\lambda)}{d\lambda} = (C_2 f_1(\lambda) f_2(1)) \int_0^{v_0} \frac{V_{12}}{f_{12}} e^{-\beta \lambda V_{12}} dv + kT \frac{d \log \overline{f_1(\lambda)}}{d\lambda} \quad (75)$$

$$kT \log \overline{f_1(\lambda)} = C_2 \int_0^\lambda \int_{v_0}^v V_{12} e^{-\beta W_1^{(1,1)}} dv dt + C_1 \int_0^\lambda \int_0^{v_0} V_{11} e^{-\beta W_1^{(1,1)}} dv dt$$

where C_1 and C_2 are the bulk concentrations of the two components in molecules per cubic centimeter. The expression 74 has been introduced only for W_1^* in the region v_0 . It could have been used for all W_i^* , but this would not be a very useful procedure. A similar equation may be constructed for $f_2(\lambda)$. Integration of equation 75 and the similar one for $f_2(\lambda)$ with regard for the fact that $f_1(0)$ and $f_2(0)$ have the value unity, leads to the result

$$\begin{aligned}\frac{1}{\bar{f}_1} - \frac{1}{f_1} &= K_1 f_2 C_2 \\ \frac{1}{\bar{f}_2} - \frac{1}{f_2} &= K_2 f_1 C_1 \\ K_1 &= -\frac{1}{kT} \int_0^1 \int_0^{v_0} V_{12} g_{12}(t, 1)^{-1} e^{-\beta t v^n} dv dt \\ K_2 &= -\frac{1}{kT} \int_0^1 \int_0^{v_0} V_{12} g_{21}(t, 1)^{-1} e^{-\beta t v^n} dv dt \\ g_{12}(t, 1) &= \frac{f_2(t, 1, q_{12}) f_1(1)}{\bar{f}_1(t)}; \quad g_{21}(t, 1) = \frac{f_{12}(1, t, q_{12}) \bar{f}_2(1)}{\bar{f}_2(t)}\end{aligned}\tag{76}$$

where all activity coefficients refer to $\lambda = 1$, since it is these that we finally desire. The functions K_1 and K_2 depend in general upon the composition of the solution. We shall assume them to be equal. It seems probable that this could be proved generally true, and it is certainly true when $e^{-\beta t v^n}$ has a strong peak at $t = 1$, the most important case. We now define quantities C_{12} and \bar{f}_{12} by the relations

$$\begin{aligned}f_1 C_1 &= \bar{f}_1 (C_1 - C_{12}) \\ f_2 C_2 &= \bar{f}_2 (C_2 - C_{12}) \\ \bar{f}_{12} &= \frac{K}{\bar{K}_1} = \frac{K}{\bar{K}_2}\end{aligned}\tag{77}$$

where K is an arbitrarily chosen equilibrium constant. Equations 77 over-define C_{12} , but substitution in equations 76 shows that both relations are satisfied. The substitution leads to the following equation for C_{12}

$$\frac{\bar{f}_{12} C_{12}}{\bar{f}_1 \bar{f}_2 (C_1 - C_{12})(C_2 - C_{12})} = K\tag{78}$$

which is the generalized mass action equation, C_{12} having a phenomenological interpretation as the concentration of compound pairs defined with reference to the equilibrium constant K . Up to this point we have made use of purely formal operations, and, except for the assumption of equality

of K_1 and K_2 , the results are rigorously true within the frame of classical statistical mechanics. While equation 78 could of course be written down at once, on formal thermodynamic grounds, our rather tedious analysis is necessary for the correlation of the activity coefficients \hat{f}_1 , \hat{f}_2 , and \hat{f}_{12} with intermolecular forces.

A suitable choice of the equilibrium constant K is evidently the following

$$K = \int_0^{v_0} (e^{-\beta v_{12}} - 1) dv$$

$$\hat{f}_{12} = \frac{\int_0^1 \int_0^{v_0} V_{12} e^{-\beta t v_{12}} dv dt}{\int_0^1 \int_0^{v_0} V_{12} g_{12}^{-1} e^{-\beta t v_{12}} dv dt} \quad (79)$$

With this equilibrium constant, we obtain simple mass action if \hat{f}_1 , \hat{f}_2 , and $\hat{f}_{12}(t, 1)$ do not deviate appreciably from unity. Again, if V_{12} has a sharp minimum of depth large relative to kT , inside v_0 , $e^{-\beta t v_{12}}$ will have a sharp peak for this configuration as well as at $t = 1$ in the interval $0 \leq t \leq 1$, and we have

$$\hat{f}_{12} = f_{12}(1, 1, q_{12}^0) \quad (80)$$

where q_{12}^0 specifies the relative coördinates of the pair at which V_{12} has its minimum. It may happen that \hat{f}_{12} , \hat{f}_1 , \hat{f}_2 do not deviate much from unity, or much less from unity than f_1 or f_2 , so that simple mass action will furnish a good first approximation in the calculation of f_1 and f_2 . This will be true for an ion pair when $-e_i e_k / \epsilon a k T$ is large relative to unity, since \hat{f}_{12} is then the activity coefficient of a dipole under the influence of ions. Again in the case of a pair of dipole molecules, for which V_{12} has a sharp minimum in the antiparallel orientation, \hat{f}_{12} will be the activity coefficient of a quadrupole in the presence of dipoles. The choice of v_0 is arbitrary. Any change in \hat{f}_{12} caused by a change in v_0 will be compensated by changes in \hat{f}_1 and \hat{f}_2 . However, the method is likely to prove useful only when V_{12} has such a deep maximum that K and \hat{f}_{12} are very insensitive to the choice of v_0 . For short-range forces, v_0 may conveniently be expanded to include the entire volume v of the solution, provided \hat{f}_{12} does not differ sensibly from unity for any configuration in which V_{12} differs effectively from zero. This is not true of interionic forces.

We shall now discuss the application of the theory just outlined to electrolyte solutions. When certain conditions are fulfilled it leads to the theory of ionic association first proposed by Bjerrum (1), and so successfully extended and applied by Kraus and Fuoss (14). Although we have considered a system of only two components, an argument similar to that used in section II allows us to apply the theory to two solute components in

the presence of an excess of solvent, V_{ik}^0 replacing the V_{ik} , and $\mu_i^0(T, p)$, the non-ideal part of the chemical potential at infinite dilution, replacing $\varphi_i(T)$ as the reference value of the chemical potential. For brevity we shall omit the superscript s on the V_{ik} in what follows. We shall consider a uni-univalent electrolyte at a molecular concentration C in a solvent of dielectric constant ϵ . The bulk concentrations of both positive and negative ions are then both equal to C . Under these circumstances, we obtain from equations 77 and 78 for the activity coefficient of either ionic species, also f_{\pm} , the mean activity coefficient,

$$\begin{aligned} f_1 &= (1 - \alpha) \bar{f}_1 \\ \frac{\bar{f}_{12} \alpha}{\bar{f}_1 \bar{f}_2 (1 - \alpha)^2} &= Kc \\ K &= 4\pi \int_0^{\infty} (e^{\epsilon^{1/2} \epsilon r k T} - 1) r^2 dr \end{aligned} \quad (81)$$

where v_0 is taken as a sphere of radius r_0 , and α is equal to c_{12}/c . For the present we suppose merely that r_0 is chosen so that W_1^2/kT is small relative to unity for all greater values of the interionic distance, so that the exponentials in equation 75 defining \bar{f}_1 may be expanded with retention of only the first two terms. For ions of the same valence type, we may suppose that for distances less than r_0 , W_1^1/kT is large and positive relative to unity so that $e^{-\beta W_1^1}$ is effectively zero, while outside r_0 the exponential may be expanded. Taking account of electrical neutrality, we then have

$$kT \log \bar{f}_1 = -\kappa^2 \int_0^1 \int_{r_0}^{\infty} [W_1^1(t, 1) - W_1^2(t, 1)] r dr dt \quad (82)$$

where κ is the Debye kappa for a uni-univalent electrolyte. It would be necessary to have recourse to equation 39 for a satisfactory investigation of W_1^2 and W_1^1 when $r > r_0$. Since this involves difficulties which have not yet been overcome, we shall limit ourselves to some semi-quantitative remarks. By analogy with the simple Debye formula, equation 58, Bjerrum assumed

$$\begin{aligned} kT \log \bar{f}_1 &= -\frac{e_1^2}{2\epsilon} \frac{\kappa'}{1 + \kappa' r_0} \\ \kappa' &= (1 - \alpha)^{1/2} \kappa \end{aligned} \quad (83)$$

where κ' is an effective kappa, computed with the concentration of "free" ions, $c - c_{12}$. This result follows from equation 82 if the potentials of average force have the form

$$W_1^1(t, 1) = -W_1^2(t, 1) = t \frac{e_1^2(1 - \alpha)}{\epsilon R} \frac{e^{-\kappa'(R-r_0)}}{1 + \kappa' r_0} \quad (84)$$

It may be verified without difficulty that $W_1^1 = e_1\psi(R)$ and $W_1^2 = -e_1\psi(R)$ where $\overline{\psi(R)}$ is the mean electrostatic potential in the neighborhood of a sphere of radius r_0 containing a total charge $te_1(1 - \alpha)$, when the Poisson-Boltzmann equation holds for $r > r_0$ and the boundary conditions of electrostatics are satisfied at $r = r_0$. This is a reasonable approximation, for $\pm e_1(1 - \alpha)$ is indeed the average charge carried by the sphere r_0 around any ion, α being the probability that an ion is "associated," that is, that another ion of opposite charge lies within the sphere, r_0 . Further, the appearance of the effective kappa, κ' , means that the other ions in the solution screen with this same average charge, $\pm e_1(1 - \alpha)$. With the Bjerrum result, equation 83, we obtain

$$\log f_1 = -\frac{e_1^2}{2\epsilon kT} \frac{\kappa'}{1 + \kappa' r_0} + \log(1 - \alpha) \quad (85)$$

where α is to be calculated by equation 81. In the original Bjerrum theory \hat{f}_{12} was assumed to be unity. Fuoss, however, has made estimates of \hat{f}_{12} by considering the interaction of an ion pair in contact with remaining "free" ions in the solution. It is difficult to judge the adequacy of Bjerrum's approximation to \hat{f}_1 . It is probably adequate in dilute solutions, when α is small relative to unity, but should be used with caution for values of α intermediate between zero and unity. When α is nearly unity, it is again adequate, for then it is sufficient to know that \hat{f}_1 is virtually unity and its form as a function of concentration is unimportant.

We have remarked that r_0 must be sufficiently large to permit the expansion of $e^{-\beta w^1}$ and $e^{-\beta w^2}$ for greater interionic distances. This condition is satisfied by Bjerrum's value

$$r_0 = e_1^2/2\epsilon kT$$

Otherwise the choice of r_0 is arbitrary, any change being absorbed in \hat{f}_{12} , \hat{f}_1 , and \hat{f}_2 . However, it should be remembered that an unfortunate choice of r_0 , for example too large a value, can make it impossible to approximate \hat{f}_{12} by unity or by the activity coefficient of a dipole consisting of an ion pair in contact. The simple Bjerrum theory will be useful only when this can be done. If $e^{-\beta w}$ has a strong peak when the ions are in contact, both K and \hat{f}_{12} are very insensitive to the choice of r_0 , provided it remains a length of molecular order of magnitude, and under these circumstances the theory leads to unambiguous results. An illuminating discussion of this point has been made by Fuoss (5), with the aid of a distribution function, specifying the probability that an ion pair be separated by a distance R , while no other ions be within the sphere of radius R .

REFERENCES

- (1) BJERRUM, N.: Kgl. Danske Videnskab. Selskab. **7**, 9 (1926).
- (2) COHN, E. J.: Annual Review of Biochemistry, Vol. IV, p. 93 (1935).
- (3) DEBYE, P., AND HÜCKEL, E.: Physik. Z. **24**, 185, 305 (1923).
- (4) FUOSS, R.: J. Am. Chem. Soc. **56**, 1027 (1934); **58**, 982 (1936).
- (5) FUOSS, R.: Trans. Faraday Soc. **30**, 967 (1934).
- (6) GUGGENHEIM, E. A.: Proc. Roy. Soc. London **148A**, (304) (1935).
- (7) HEITLER, W.: Ann. Physik [4] **80**, 630 (1928).
- (8) HILDEBRAND, J. H., AND WOOD, S. E.: J. Chem. Physics **1**, 817 (1933).
- (9) HILDEBRAND, J. H.: Chem. Rev. **18**, 315 (1936).
- (10) KEESOM, W. H.: Physik. Z. **22**, 129, 643 (1921).
- (11) KIRKWOOD, J. G.: J. Chem. Physics **3**, 300 (1935).
- (12) KIRKWOOD, J. G.: J. Chem. Physics **2**, 767 (1934).
- (13) KIRKWOOD, J. G.: J. Chem. Physics **2**, 351 (1934).
- (14) KRAUS, C., AND FUOSS, R.: J. Am. Chem. Soc. **55**, 476, 1019, 2837, 3614 (1933).
- (15) LEVINE, S.: Proc. Roy. Soc. London **152A**, 529 (1935).
- (16) ONSAGER, L.: Chem. Rev. **13**, 73 (1933).
- (17) SCATCHARD, G.: Chem. Rev. **8**, 321 (1931).
- (18) SCATCHARD, G.: Physik. Z. **33**, 22 (1932).

CONCENTRATED SOLUTIONS OF STRONG ELECTROLYTES¹

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The limiting law of the Debye theory of strong electrolytes (7) is now firmly established. As experimental technique improves, the measurements agree better and better with the theory. The extension to concentrated solutions is more difficult, because many specific properties of the ions must be taken into account. Much progress can be made, however, both in the rational expression of the properties of solutions of simple ions and in the application of a few general principles to give treatments of the properties of solutions of mixtures in terms of the properties of solutions of their components which are very useful in the study of chemical equilibria.

The limiting law depends only on the valences of the ions, the temperature, and the dielectric constant of the solvent. In more concentrated solutions the sizes of the ions and their effects on the dielectric constant must be taken into consideration. The latter is not the effect on that dielectric constant measurable by macroscopic instruments, which is an increase due to the electrostatic interaction between the ions (10, 38, 39), but is the effect on the microscopic dielectric constant, which is a much smaller decrease due largely to the displacement of the solvent (29). Recently Wyman (40) has shown that the dielectric constants of polar and non-polar mixtures are proportional to the concentrations of the polar liquids, and Onsager (21) appears to have explained this finding theoretically. If this is also true for the microscopic dielectric constant of electrolyte solutions, then the square of the reciprocal thickness of the ion atmosphere, κ^2 of the Debye theory, is proportional, not to the number of ions in unit volume of the solution, but rather to the number in unit volume of the solvent, or, at constant temperature and pressure, to the number in unit weight of the solvent. This relation simplifies greatly the correlation of the theory with thermodynamic treatments. We should not expect the relation to be exact, but it is certainly very much better than the one usually

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made that the ions do not affect the dielectric constant. Those who have felt themselves forced to use ionic strengths in moles per liter of solution because the theory demands it, may be relieved to know that a much better theory demands that the ionic strength be in moles per unit quantity of solvent.

Not only does the electrostatic interaction between the charges depend upon the sizes of the ions and their effects on the dielectric constant of the solution in concentrated solutions, but there are also other interactions between ions which correspond to the salting out of non-electrolytes and to the deviations of purely non-electrolyte solutions from the ideal solution laws. The exact treatment would require the insertion of three kinds of energy in the statistical expressions and would give equations much too complicated for solution. To obtain an approximate solution we assume that the distribution of the ions is determined solely by the electrostatic interaction of their charges and, except in the calculation of the "higher terms" of Bjerrum (6) and Gronwall and LaMer (12), we assume the Debye-Hückel first approximation for this distribution. Then the total ion concentration is independent of the distance from the central ion, but the fraction of this concentration made up of ions with charges of the same sign as that of the central ion is very small in the neighborhood of the central ion. We assume that it is zero for all distances at which the short range interactions come into play. This is exactly the basic assumption of Bjerrum's theory (4, 5) of "specific ion interaction."²

Using the methods of Debye and his colleagues for the charge-charge interaction (7) and the "salting out" (8, 19), and my own expression for the non-electrolyte term (28), we obtain the following expression for the non-ideal free energy per mole of ion of a solution of two kinds of ions.

$$\frac{F - F_I}{\nu_s N_s} = \frac{\epsilon^2 N}{2D_0} \left[z_1 z_2 X + z_1 z_2 X V_s m + \frac{2 \nu_1 \nu_2}{\nu_s} \left(\frac{V_2 z_1^2}{b_1} + \frac{V_1 z_2^2}{b_2} \right) m \right] + \frac{A m}{1 + V_s m}$$

in which $F - F_I$ is the non-ideal free energy of the system; N_s is the number of moles of electrolyte; ν_1 and ν_2 are the numbers of ions of the two kinds per molecule of electrolyte, z_1 and z_2 their valences, one of which must be negative, and V_1 and V_2 their molal volumes; ϵ is the electronic charge; N is Avogadro's number; N_0 is the number of moles of solvent,

² An expression for the thermodynamic properties of electrolyte solutions including the non-electrolyte effects was published by the author some years ago (29). It differed from the present expression in that the relation between the volume and the effect on the dielectric constant was left arbitrary and that the distribution of the ions was considered uniform for the calculation of the "salting out" and the non-electrolyte terms. The expression given here is believed to be a considerable improvement.

V_0 is its molal volume, and D_0 its dielectric constant; b_1 and b_2 are the radii of the two ions effective for salting out. The other symbols are defined in the following equations, in which a is the sum of the two radii effective in collisions between ions, and a_{12} , a_{10} , and a_{20} are the mutual cohesive energy densities.

$$m = N_s/V_0N_0$$

$$\nu_s = \nu_1 + \nu_2$$

$$V_s = \nu_1V_1 + \nu_2V_2$$

$$D = D_0V_0N_0/V$$

$$\kappa^2 = -\frac{8\pi N^2\epsilon^2z_1z_2\nu_sN_s}{1000 RTDV} = -\frac{8\pi N^2\epsilon^2z_1z_2\nu_s m}{1000 RTD_0}$$

$$X = \frac{\kappa}{1 + \kappa a} - Y$$

$$Y = \left[1 + \kappa a - \left(\frac{1}{1 + \kappa a} - 2 \ln (1 + \kappa a) \right) \right] / \kappa^2 \epsilon^3$$

$$A = 2\nu_1\nu_2V_1V_2(2a_{12} - a_{10} - a_{20})/\nu_s$$

The first term in the brackets is nearly the same as the Debye-Hückel expression for the charge-charge interaction for constant dielectric constant. It is negative and initially proportional to the square root of the concentration, but the slope decreases so rapidly with increasing concentration that the effect of the difference between κ and κ_0 of Debye and Hückel is very small. The second term represents the effect of the changing dielectric constant on the charge-charge interaction. It is also negative and is proportional to the first term times the concentration. The last term in the brackets represents the charge-molecule part of the "salting out." It is usually positive, and is proportional to the concentration at all concentrations. The term outside the brackets represents the non-electrolyte molecule-molecule interaction, which is usually negative. It is initially proportional to the concentration, but the slope decreases as the concentration increases. Wyman's theory of the dielectric constant is used whenever D_0 , κ , X , or Y appear in an equation. Brønsted's specific ion interaction is used to determine a from the sum of the two effective ion radii alone for the charge-charge term, to substitute $2(V_2z_1^2/b_1 + V_1z_2^2/b_2)$ for

$V_s(z_1^2/b_1 + z_2^2/b_2)$ in the charge-molecule term, and to substitute $2\nu_1V_1\nu_2V_2$ for V_s^2 in the molecule-molecule term.

It may surprise you to see the charge-molecule effect given by the expression which corresponds to the Debye-MacAulay (8) salting-out equation rather than to the modified expression of Debye (9), particularly since we have recently shown that the experimental salting-out results agree with the latter (36). This choice is correct, however, and follows from our assumption that the distribution is determined solely by the charge-charge interactions.

With this expression for the non-ideal free energy we have no further need of approximations. The other quantities may be calculated from it exactly by thermodynamics alone. The equations for the logarithm of the activity coefficient, $\ln \gamma$, and for the osmotic coefficient, ϕ , follow.

$$\begin{aligned} \ln \gamma = & -\ln(1 + \nu_s N_s/N_0) + \frac{\epsilon^2 N}{2RTD_0} \left[\frac{z_1 z_2 \kappa}{1 + \kappa a} + \left(\frac{\kappa}{1 + \kappa a} + X \right) z_1 z_2 V_s m \right. \\ & \left. + \frac{4\nu_1 \nu_2}{\nu_s} \left(\frac{V_2 z_1^2}{b_1} + \frac{V_1 z_2^2}{b_2} \right) m \right] + \frac{Am(2 + V_s m)}{RT(1 + V_s m)^2} \\ \phi = & \frac{\ln(1 + \nu_s N_s/N_0)}{\nu_s N_s/N_0} + \frac{\epsilon^2 N}{2RTD_0} \left[z_1 z_2 Y + \frac{z_1 z_2 \kappa V_s m}{1 + \kappa a} + \frac{2\nu_1 \nu_2}{\nu_s} \left(\frac{V_2 z_1^2}{b_1} + \frac{V_1 z_2^2}{b_2} \right) \right] \\ & + \frac{Am}{RT(1 + V_s m)^2} \end{aligned}$$

In each the first term gives the value for ideal solutions, which is approximately $-0.018 \nu_s m$ for $\ln \gamma$ and approximately $1 - 0.009 \nu_s m$ for ϕ . The other terms correspond to the free energy equation in order, and have the same sign in each equation. If the slope is strictly proportional to some power of m in the free energy equation it is in the others also; if the slope decreases with increasing concentration it decreases more rapidly in the equation for $\ln \gamma$ and still more rapidly in the equation for ϕ .

The equations for $\ln \gamma$ and ϕ are not very much more complicated than the approximate equations of Hückel (19), which are given by taking the first term and the first and third terms in the bracket, using the volume of the solution rather than that of the solvent in the terms in the bracket, and giving another definition to the constant coefficient in the third term. The added complication of the second term in brackets and the last term is partially compensated by the more convenient concentration units. These equations also have the advantage that they are thermodynamically consistent.

The Bjerrum-Gronwall-LaMer "higher term correction" is omitted

from the above equations. The Gronwall-LaMer expressions (12) for $\ln \gamma_h$ and ϕ_h for the case that $z = z_1 = -z_2$ are:

$$\ln \gamma_h = - \sum_{n=1}^{\infty} \left[\frac{N\epsilon^2 z^2}{RTD_0 a} \right]^{2n+1} (1 + V_s m)^{2n+1} \left[\left(\frac{X_n}{2} - 2n Y_n \right) + V_s m \left(Y_n - \frac{V_s m X_n}{2} \right) \right]$$

$$\phi_h = - \sum_{n=1}^{\infty} \left[\frac{N\epsilon^2 z^2}{RTD_0 a} \right]^{2n+1} (1 + V_s m)^{2n} \left[\frac{X_n}{2} - (2n+1) Y_n + \frac{V_s m X_n}{2} \right]$$

in which X_n and Y_n have the same meanings as in the original paper.

This treatment might be extended to the heat and volume changes on dilution and to their temperature and pressure derivatives, but the temperature and pressure derivatives of so many parameters are involved that it seems advisable to omit this extension for the present. For the equations given above we need know only the temperature, the molal volume and dielectric constant of the solvent, the valence, molal volume in solution, and radius effective in salting out for each ion, the effective collision diameter a of the pair of ions, and their molecule-molecule interaction coefficient, A . The alkali and halide ions may be assumed spherical, and we shall use the values of their radii determined by Pauling (22) from the crystal lattices.³ For spheres $b = r$ and $a = r_1 + r_2$. The volume in solution may be expected to be somewhat less than four times the actual volume of the molecules, $4\pi r^3/3$, and the constant A may be assumed to be the same for all the alkali halides and may be expected to be about the same as that for the aliphatic hydrocarbons in water.

We shall make the comparison with the experimentally determined osmotic coefficients, which have the advantages over the activity coefficients of the solutes that they may be determined for a much larger number of solutions and that they involve no extrapolation to zero concentration. Freezing-point measurements give the most accurate values of the osmotic coefficients, but they have the disadvantage that they are not isothermal. For concentrated solutions measurements of vapor pressure or by the isopiestic or isotonic method are much superior. Of these the latter are considerably more accurate. We shall use the measurements of Sinclair and Robinson by this method, but we shall use as standard our curve for sodium chloride, which appears to me much better established than that of potassium chloride. Our measurements of the relation of the osmotic coefficient of potassium chloride to that of sodium chloride check theirs very closely. They have made measurements with all the alkali chlorides,

³ These values in Ångström units are: Li, 0.574; Na, 0.873; K, 1.173; Rb, 1.294; Cs, 1.434; F, 1.225; Cl, 1.589; Br, 1.702; I, 1.867.

bromides, and halides up to saturated solutions or to solutions isotonic with saturated potassium chloride.

We cannot be satisfied with approximate values of the ratio of the volume in solution to the actual volume of the ions or of the non-electrolyte reaction coefficient, A , but each of these quantities must be determined more precisely than the osmotic coefficient itself. They were therefore determined from the osmotic coefficients of 1 molal lithium bromide and cesium bromide. The volume so determined is $0.008r^3$ if the volume is in liters per mole and r in Ångström units, which is 3.15, or somewhat less than four, times the actual volume of the molecules. This value for the volume leads to $A/RT = 0.0089 r_1^3 r_2^3$, which is one-third the value for an aliphatic

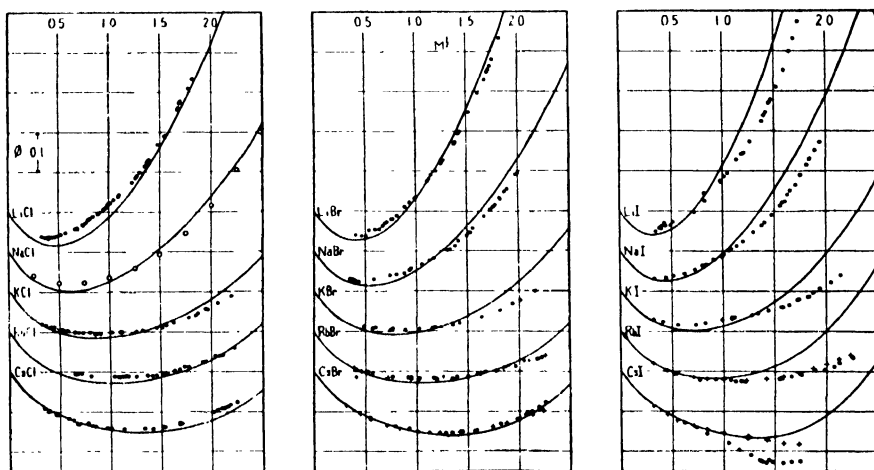


Fig. 1. Osmotic coefficients of alkali halides at 25°C.

hydrocarbon in water. Of the two parameters whose exact values must be determined from the experimental data, one corresponds very closely to the expected value, the other only approximately so. The agreement is perhaps as good as should be expected, for the calculated values depend upon an unjustified extension of the theory of non-polar mixtures, and our treatment is such that an error in any of our other approximations is carried over to this parameter. For example, a small error in the volume ratio given above would be doubled in the calculation of A .

In figure 1 the curves represent the calculated values of the osmotic coefficients and the dots represent the published experimental results of Robinson and Sinclair (23, 24). For sodium chloride the circles represent our choice (37) of the most probable curve through the results from elec-

tromotive force and vapor pressure determinations. Our curve was also influenced by measurements on potassium chloride, sulfuric acid, sucrose, and α -methylglucoside. For rubidium bromide and iodide the crosses represent experimental measurements reported privately by Dr. Robinson (26), and for the cesium salts the crosses are his smoothed values from new measurements. The differences between the crosses and circles are small except for cesium iodide, but wherever there is any difference the crosses should be accepted.

The curves for lithium bromide and cesium bromide, which are made to fit the experimental points at 1 molal, show very satisfactory agreement throughout, if we consider that there are only two arbitrary parameters for the two curves. The agreement is about as good for the other chlorides and bromides, although they were not used at all in the determination of the parameters. The calculated values for dilute solutions with small ions are distinctly low. There is also a tendency, increasing from chlorides through bromides to iodides, for the calculated values to be too high in concentrated solutions. On the whole, however, the agreement is very satisfactory.

It would be entirely legitimate to tinker with the calculated results to give better agreement with the measurements. Pauling's ionic radii are only approximate, and there is no reason to suppose that the radii in solution are exactly the same as those in the crystal lattices. A slight increase in the sizes of the smaller ions would greatly improve the fit in dilute solutions. It is impossible to predict whether such a change would also remedy the difficulties in concentrated solutions. It might be necessary to alter the molecule-molecule term also so that it remains more nearly proportional to the concentration to correspond to the behavior of less polar solutes in water rather than to the too simple theory. It seems advisable for the present, however, to determine from the properties of the solutions only those parameters which are absolutely necessary, and to be satisfied with this approximate agreement.

These results do show that the alkali and halide ions are characterized by their valences and sizes alone. The decrease of the osmotic coefficient with increasing size of the cation for the chlorides, bromides, and iodides and the decrease with increasing size of the anions for the cesium salts are explained by the facts that the term for the charge-charge interaction is of secondary importance in concentrated solutions and that the deviation of the osmotic coefficient from unity is not far from the difference between the salting-out term and the non-electrolyte term. The first of these is largest when one ion is small and the other large; the second becomes more important when both ions are large. The theory does make the osmotic coefficients of the rubidium salts increase with increasing size of the anion

like those of the lithium, sodium, and potassium salts, while the experimental osmotic coefficients decrease like those of the cesium salts. The calculated increase and the measured decrease are both so small, however, that the difference in sign is unimportant. The theory also agrees with the freezing-point measurements (11) in making the osmotic coefficients of the fluorides increase with increasing size of the cation in the opposite order to those of the other halides. Quantitative agreement would require a larger radius for the fluoride ion than that given by Pauling, for the calculated potassium, rubidium, and cesium curves are all about the same as that of cesium chloride, and Lannung's direct vapor-pressure measurements (20) indicate that they should be about the same as that of sodium bromide.

The application of this method to polyatomic ions is considerably more complicated, for such ions cannot be assumed to be spherical and several parameters for each ion must be determined from the properties of the solutions. There are at least two types of variations from the behavior of the halides (31). The hydroxides behave very much as the fluorides, and the formates and acetates behave as though a , b , and A were about the same as for the fluorides, but V were very much larger. The nitrates, chlorates, and perchlorates, on the other hand, behave as though a , b , and V were about the same as for the bromides, but A were very much larger. The application to mixtures is even more complicated, largely because the presence of two kinds of cations, or two kinds of anions, with different sizes makes the expressions for the interaction of the ionic charges very much more complicated (29).

We may make considerable progress, particularly in the study of mixtures, without such a detailed treatment. We start with the very general result of statistical mechanics that that part of the non-ideal free energy per unit quantity of solution which is contributed by short range forces may be expressed as a multiple integral power series in the molalities of the various components. We use also the result of the Debye-Hückel theory that the effect of the long range forces between the ionic charges requires a multiple power series containing the square root of the ionic strength as well as the concentration of each component, and we combine the two to give the following series, in which the numerical values of the A 's are given by the Debye-Hückel theory (33, 34):

$$\begin{aligned} \frac{F - F^*}{RT} = & \sum_i N_i \left(\ln \frac{N_i}{w_0 N_0} - 1 + A_i \sqrt{I} \right) + \sum_{ij} \frac{N_i N_j}{w_0 N_0} (B_{ij} + C_{ij} \sqrt{I}) \\ & + \sum_{ijk} \frac{N_i N_j N_k}{w_0^2 N_0^2} (D_{ijk} + E_{ijk} \sqrt{I}) + \end{aligned}$$

N_i is the number of moles of ions of the i^{th} component in the system, N_0 is the number of moles of the solvent, and $w_0 N_0$ is unit mass of solvent; I is twice the ionic strength in moles per unit mass of solvent. The B 's, C 's, D 's, and E 's are determined by the properties of the solution. The following expressions for the activity coefficients and the osmotic coefficient are obtained from the free energy expression by thermodynamics alone.

$$\begin{aligned}\ln \gamma_p &= \frac{3}{2} A_p \sqrt{I} + 2 \sum_i B_{ip} m_i + \left(2 \sum_i C_{ip} m_i + \frac{z_p^2}{2I} \sum_i C_{ij} m_i m_j \right) \sqrt{I} \\ &+ 3 \sum_{ij} D_{ijp} m_i m_j + \left(3 \sum_{ij} E_{ijp} m_i m_j + \frac{z_p^2}{2I} \sum_{ijk} E_{ijk} m_i m_j m_k \right) \sqrt{I} + \dots \dots \dots \\ \phi &= 1 + \frac{1}{2} \sqrt{I} \sum_i A_i x_i + M \sum_{ij} (B_{ij} + \frac{3}{2} C_{ij} \sqrt{I}) x_i x_j \\ &+ M^2 \sum_{ijk} (2D_{ijk} + \frac{5}{2} E_{ijk} \sqrt{I}) x_i x_j x_k + \dots \dots \dots\end{aligned}$$

in which $m_i = N_i/w_0 N_0$, $M = \sum_i m_i$, $x_i = m_i/M$.

There is no theory which tells us that these series must converge conveniently. In fact they will be divergent if there is a fairly large amount of chemical combination or any other interaction which is limited to a pair of molecules or ions, such as that described by the "higher term correction." This difficulty could probably be remedied by adding to each term in the concentrations another coefficient times the logarithm of the ionic strength, but there are as yet no experimental data to warrant this extension. If an interaction is not limited to two molecules its effect may be large and still lead to convenient convergence. We have found that the freezing-point depressions of most uni-univalent electrolytes may be represented up to concentrations of 1 molal by the five terms given above, and I shall show later that no type of series can be simpler than this one with four terms.

For a single solute these equations have little advantage over graphic methods, provided that the latter also make use of the Debye limiting law. For mixed solutes, on the other hand, the gain is enormous. We made about thirty determinations for each single salt (35). To cover the field as completely would require four hundred fifty determinations for a binary mixture, forty-five hundred for a ternary mixture, and almost thirty-four thousand for a reciprocal salt pair, and the graphical treatment of the results would be a stupendous task. The use of these equations reduced the measurements needed to one one-hundredth, and probably reduced the labor of handling the data more than that.

A still further gain for mixtures is obtained from the assumption that the short range forces between two ions with charges of the same sign may

be neglected unless there is a third ion of the opposite sign in their immediate neighborhood. Then the B and C coefficients for any mixture can be determined from the single salt solutions, and the D and E coefficients can be determined from the single salt solutions and one solution of each mixture with a common ion.

The most comprehensive test of the application of this method to mixtures is our own study of the freezing-point depressions of mixtures of potassium nitrate, potassium chloride, lithium nitrate, and lithium chloride

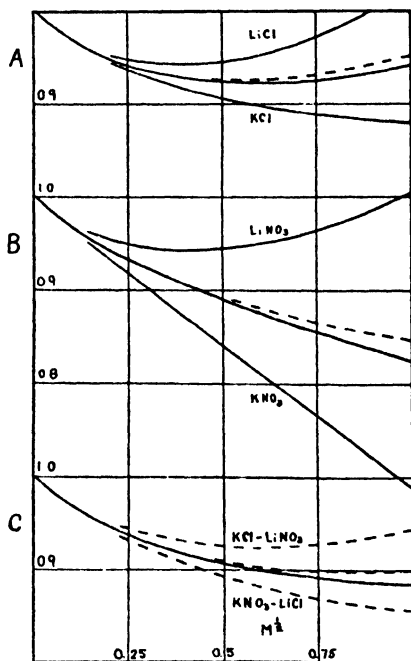


FIG. 2. Osmotic coefficients of mixtures at 0°C . A, KCl-LiCl ; B, $\text{KNO}_3\text{-LiNO}_3$; C, KCl-LiNO_3 or $\text{KNO}_3\text{-LiCl}$.

(35). The series, simplified as described in the last paragraph, describe the measurements exactly. Since this method requires very precise and comprehensive measurements which are not yet available in any other case, we shall be more interested in the conclusion that all the parameters may be determined approximately from measurements on single salts alone. If they were exactly determined the osmotic coefficients of mixtures with a common ion would be additive. Figure 2A shows the osmotic coefficients of potassium chloride, lithium chloride, and their 1-1 mixture, plotted against the square root of the molality. The broken curve is the

mean of the curves for the two salts. It agrees closely with the experimental curve for the mixture in dilute solutions as our theory demands, and the difference is not very great even at 1 molal. Figure 2B shows about the same agreement for potassium nitrate, lithium nitrate, and their 1-1 mixture in spite of the greater spread between the two salts. I shall omit the curves for the mixtures potassium nitrate-potassium chloride and lithium nitrate-lithium chloride, for they show no difference between the calculated results and the measurements up to 1 molal, which is the limit of our measurements. Figure 2C shows the 1-1 mixture of potassium nitrate and lithium chloride, which is also the 1-1 mixture of potassium chloride and lithium nitrate. The lowest broken curve is the mean of the curves of the first pair, and the highest is the mean of those of the second pair. Neither agrees well with the experimental curve. Our theory demands, however, that in this case without a common ion the curve be given by the mean of those for all four salts of the reciprocal salt pair. This is given by the middle broken curve, which agrees with the experimental measurements about as well as those in which only the anion is changing.

It is not at all necessary to represent the Debye-Hückel limiting law by a term proportional to the square root of the ionic strength, but any function of the ionic strength which reduces to this in very dilute solutions may be substituted. Ever since Hückel's first paper on concentrated solutions (19), attempts have been made to find some function of the ionic strength depending only on the valence type, the individual deviations from which should be proportional to the concentration. If there were any such function the osmotic coefficients of mixtures with a common ion would be strictly additive at all concentrations; so figure 2 shows that such a function cannot exist. We will also see from measurements on single salts that such a function is impossible. Nevertheless, it is very convenient to subtract from the logarithm of the activity coefficient the Debye-Hückel limiting law divided by 1 plus the square root of the ionic strength

$$Az_1z_2 \sqrt{\mu}/(1 + \sqrt{\mu})$$

The corresponding expression for the osmotic coefficient is

$$1 + Az_1z_2 [1 + \sqrt{\mu} - 1/(1 + \sqrt{\mu}) - 2 \ln (1 + \sqrt{\mu})]/\mu$$

The next figures show as $\Delta\phi$ the deviations of the osmotic coefficients from this function plus a term linear in the ionic strength. Figure 3 gives $\Delta\phi$ up to 1 molal determined from freezing points for potassium nitrate (30), potassium chloride (31), and potassium acetate (32). It shows that this function is a convenient one from which to plot deviations, but that

these deviations are much larger than the experimental errors. It also shows conclusively that no other function common to all three salts will reduce the deviations of all of them. Figure 4 shows $\Delta\phi$ for the same salts up to 3.5 M , determined from the isotonic measurements of Robinson and Sinclair (23,25) at 25°C. and our curve for the osmotic coefficient of sodium chloride. It confirms the conclusions from the previous figure, and shows that these do not depend on the temperature variation in the freezing-point method.

Figure 5 illustrates the complications that may be expected with salts of higher valence type, or with solvents of lower dielectric constant than water. It shows $\Delta\phi$ determined by the isotonic method at 25°C. for magnesium, manganese, nickel, zinc, copper, and cadmium sulfates by Robin-

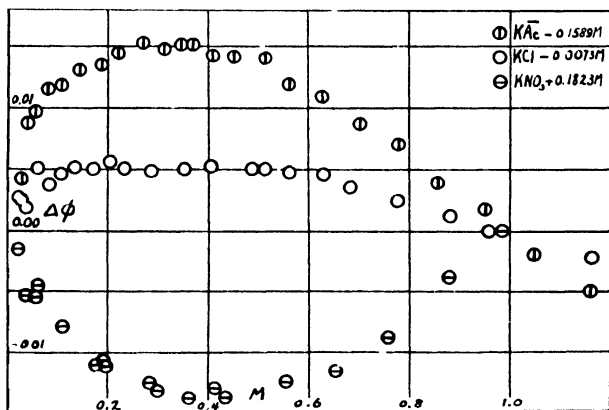


FIG. 3. Deviations of osmotic coefficients at 0°C.

son and Jones (26). The linear term is 0.1 M in all cases. It may appear that the differences between these curves and any one of them taken as standard would be more nearly proportional to the concentration than the deviations shown here, but the actual gain is very small. All of the curves are positive in dilute solutions and must come to zero very steeply. Moreover, if the theory of "higher terms" is even qualitatively correct, they should all be negative in very dilute solutions, and they must therefore descend very rapidly with decreasing concentration and then rise still more steeply. Hausrath (18) has measured the freezing-point depressions in very dilute solutions of all but manganese sulfate, and his measurements yield negative values of $\Delta\phi$, more negative for those salts whose values are lower in this figure. The insert shows the first two points of Robinson and Jones for magnesium sulfate and also $\Delta\phi$ from the freezing-point measurements of Hall and Harkins (14). The scale of ordinates of

this inset are the same as in the main figure, but the scale of abscissas is magnified ten times. The agreement of the two series in the more concentrated solutions is as good as could be expected at such different tem-

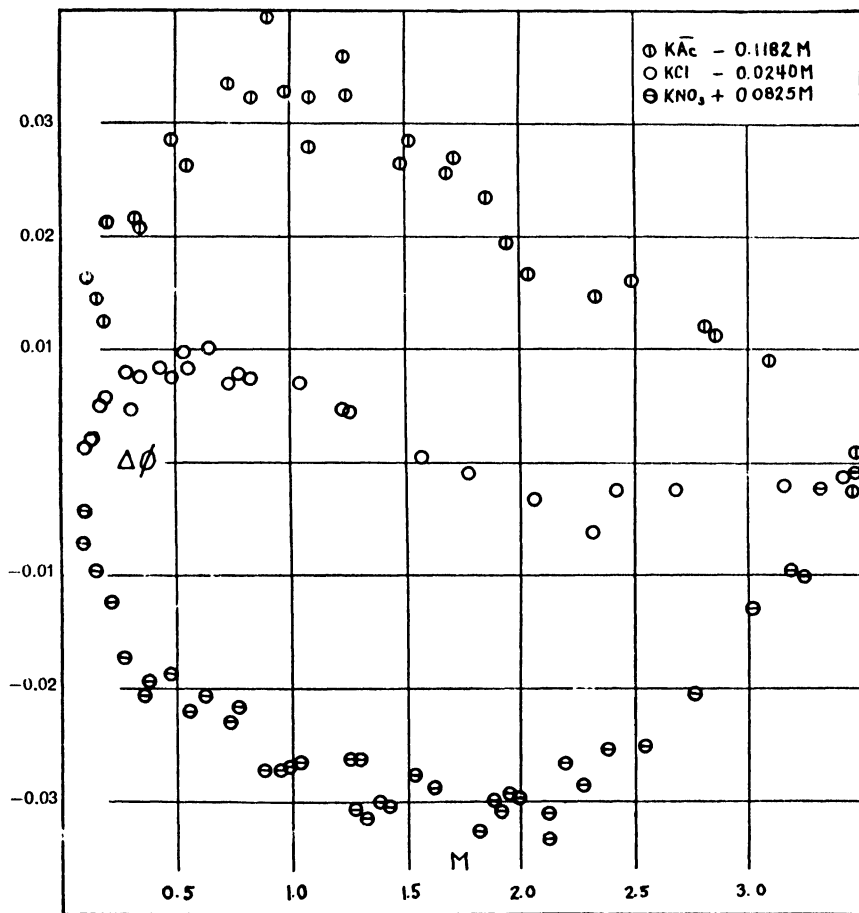


FIG. 4. Deviations of osmotic coefficients at 25°C.

peratures. In more dilute solutions the freezing points yield negative values of $\Delta\phi$, in agreement with Hausrath's measurements and the theory.

Similar expressions for the logarithm of the activity coefficient have frequently been used, and always with the assumption that the term corresponding to our $\Delta\phi$ is zero. The expression used by Hückel (19) and by Harned and Åkerlöf (15, 16) for hydrochloric acid and the alkali chlo-

rides differs only in the inclusion of the ideal solution expression as in our first equation, in the expression of the ionic strength per unit volume of solution rather than of solvent, and in the use of a constant k greater than unity in the expression $1 + k\sqrt{\mu}$. Guggenheim (13) has extended the use of their expression, changed only by making k unity, to all strong electrolytes. Instead of subtracting the ideal solution term for the osmotic coefficient, Guggenheim invents a new osmotic coefficient for which this subtraction is unnecessary. This is somewhat less convenient than our

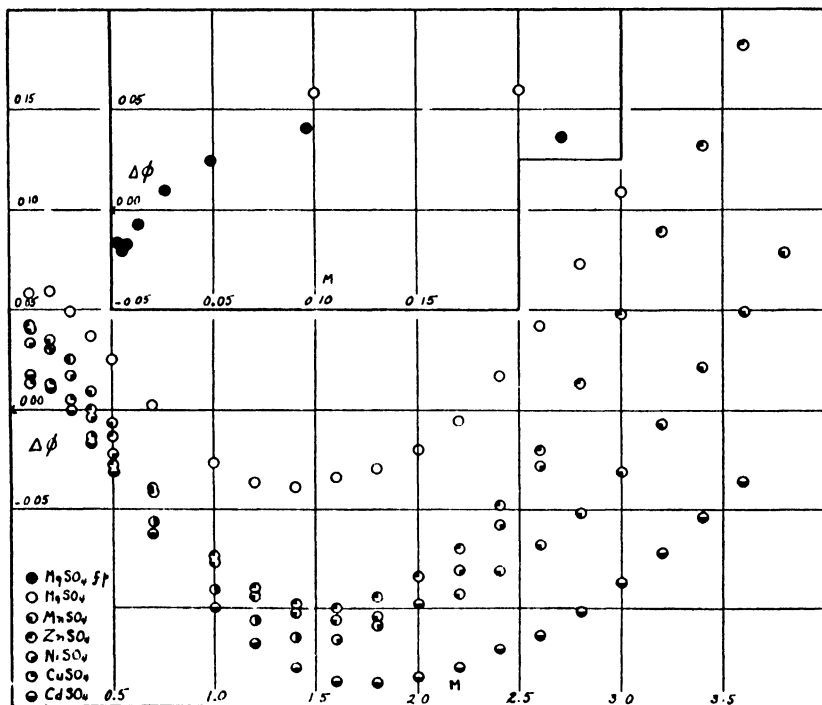


FIG. 5. Deviations of osmotic coefficients of sulfates of bivalent metals

form, but not seriously so. However, in the calculation of activity coefficients of the solute from the osmotic coefficients, he uses thermodynamic relations which are exact for our coefficients but only approximate for his. This sacrifice of exact thermodynamics seems quite inexcusable. Guggenheim limits the use of his expression to ionic strengths less than 0.1 molal, and appears to consider the expression exact within these limits. An examination of figure 3 shows that a straight line through the point at 0.1 molal will not miss seriously any of the points in more dilute solutions,

but that the best smooth curve through all the points shows considerable curvature below 0.1 molal and differs from the straight line by an amount which is not unimportant in the calculation of the activity coefficient of the solute by integration. With salts of higher valence type the discrepancy is still more serious. Guggenheim claims that the measurements of Hall and Harkins are fitted by his expression up to 0.025 M , and the error which he ascribes to the measurements is not many times those made by these observers with other solutes. An examination of figure 7 shows, however, that a straight line through the point at 0.025 M intersects the best smooth curve through all the measurements almost at right angles.

Åkerlöf (1, 2, 3) uses as norm the experimental curve for hydrochloric acid, and assumes that the deviations for other electrolytes are proportional to the ionic strength in moles per unit quantity of solvent. For uni-univalent electrolytes this corresponds closely to the use of our expression, with k considerably larger than unity. For other valence types his treatment is contrary to the Debye-Hückel theory and to experiment.

Although the relation is inexact as we have just seen, it is often convenient to assume as an approximation that $\Delta\phi$ and the corresponding expression for the logarithm of the activity coefficient are zero. It is still more convenient, and at the same time more accurate, to make two other approximations which would be exact if there were any such function and if Brønsted's theory (4, 5) of "specific interaction" were exact. If all the ions have the same absolute value for the ionic charge, these two assumptions are sufficient. If they have not, there is an ambiguity which may be removed by treating the ions as independent components. It is therefore convenient to express our approximations in terms of the individual ion activities, although we shall use them only in such combinations that the addition or removal of the corresponding ions leaves the solution electrically neutral. We shall assume that

$$\ln \gamma_k = \frac{-Az_k^2\sqrt{\mu}}{1 + \sqrt{\mu}} + \sum_j f_{kj}(\mu)m_j$$

in which μ is the ionic strength, A is given by the Debye-Hückel limiting law, z_k is the valence of the k^{th} type of ion, m_j is the molality of the j^{th} ion species. If the expression corresponding to $\Delta\phi$ were zero, $f_{kj}(\mu)$ would be independent of the ionic strength, so we know that it varies only slowly with the ionic strength. The use of a function of the ionic strength rather than of the concentrations of all the solutes makes $\ln \gamma$ a linear function of the composition at constant ionic strength. This relation has been shown, particularly by Harned and his coworkers (17), to hold almost within the experimental error up to the highest concentrations studied. If $f_{kj}(\mu)$ is strictly constant, it is zero by Brønsted's theory of "specific

ion interaction," if the j and k ions have charges of the same sign; $f_{kj}(\mu)/z_k = f_{jk}(\mu)/z_j$ by the condition of integrability, assuming the ions to be independent components, if z_k and z_j have opposite signs; and $f_{kj}(\mu) = f_{jk}(\mu)$ by the same condition if either z_k or z_j is zero. We may extend these relations as approximations even to concentrated solutions.

If both ions have the same absolute value of the charge, it follows that the activity coefficients of the two ions are equal to each other and to the mean activity coefficient in a solution of a single salt. In a solution of another salt of the same valence type, the mean activity coefficient is the geometric mean of those of the solute salt and of the solvent salt if they have an ion in common, and it is the geometric mean of those of the

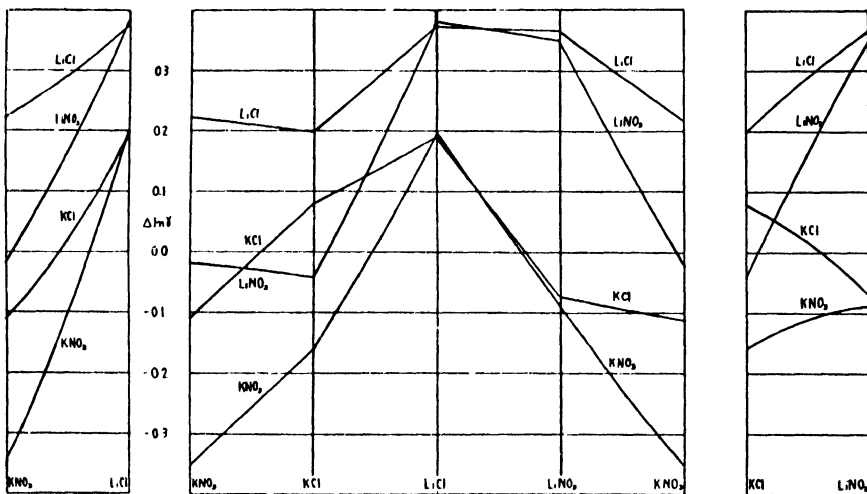


FIG. 6. Deviations of logarithms of activity coefficients at constant ionic strength of unity.

reciprocal salt pair if there is no common ion. In the case of ions with different absolute values of the valence the relations are more complicated, because the first part of the expression is proportional to the square of the valence, and the second part is proportional to the absolute value of the valence, but the relations are given just as definitely by the assumptions we have made. The important result of these assumptions is that the activity coefficients of any salt in any salt mixture may be determined from measurements on single salts alone.

In case the solubility is too limited to permit the determination of the activity coefficients from measurements on solutions of the salt itself, they may be determined by measurements with a single mixture and the use of

the above approximations. If there are not enough measurements to use the above principles, the functions of the ionic strength may be taken as contents with sufficient accuracy for many purposes. This corresponds closely to Åkerlöf's treatment of uni-univalent electrolytes (1). If there are no measurements at all with the salts in question, the magnitude of the functions may be estimated from the behavior of other similar salts.

If either z_k or z_j is zero, the function $f_{jk}(\mu)$ can be determined only from measurements on mixtures, or from theoretical considerations. The terms for the individual ions cannot be separated, but as long as the function is

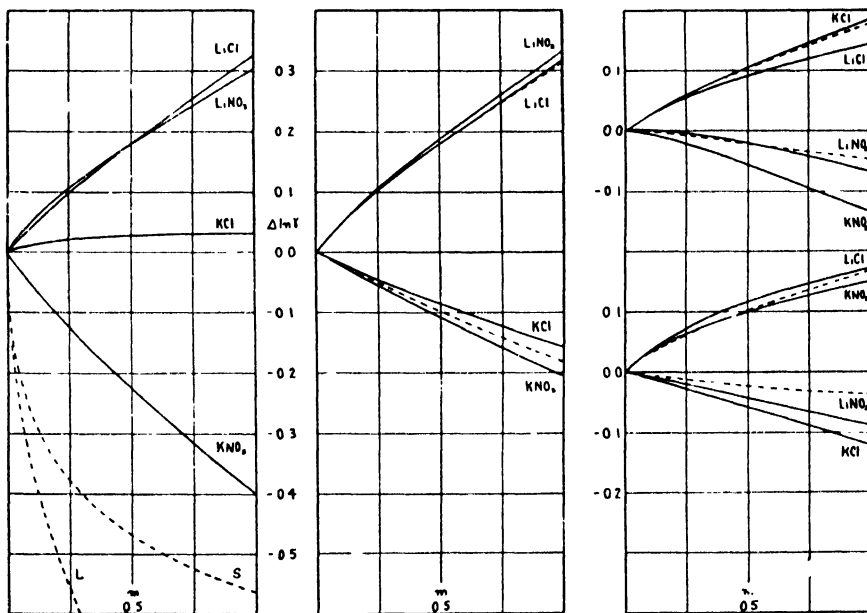


Fig. 7. Deviations of logarithms of activity coefficients at constant composition of solute.

strictly constant, it must be additive for the ions. For the distribution of either electrolyte or non-electrolyte between the solution and another phase, our treatment tells us only that the logarithm of the activity coefficient is nearly proportional to the concentration of the other species. For homogeneous chemical equilibria it is helpful to make another approximation. If there is a reaction $A + B = C$, we assume that $f_{c_j}(\mu) = f_{a_j}(\mu) + f_{b_j}(\mu)$. If either z_a or z_b is different from zero, this assumption is contradictory to those we have made concerning the relation of these functions to the valence, but there are compensating errors which should make it fairly satisfactory in spite of that fact.

Many of these assumptions may be tested only in isolated cases which would require too much space for presentation. The application to mixtures of uni-univalent electrolytes in aqueous solution may be tested from the activity coefficients determined by the freezing-point measurements on mixtures of potassium nitrate, potassium chloride, lithium nitrate, and lithium chloride discussed above (35). The results are all expressed as deviations from the first term in the logarithm of the activity coefficient given above, $\Delta \ln \gamma$. Figure 6 shows the second term for each of the four salts in all the possible binary mixtures at a constant ionic strength of 1 molal. The mixtures with a common ion are in the center and those without are at the sides. It shows that the logarithm of the activity coefficient is very nearly a linear function of the composition even in these concentrated solutions. None of these curves is a straight line, but the deviations are so small as to be scarcely visible in most, and the assumption of linearity would produce no great error in any of them.

Figure 7 shows $\Delta \ln \gamma$ versus the molality at constant composition. The left-hand side gives as full curves the results for the four salts, each in its own solution. The broken curves are the Debye limiting law (*D*) and the first term, or standard from which the deviations are calculated (*S*). In the rest of the figure a full line represents $\Delta \ln \gamma$ for the salt indicated on the curve in a solution of the salt indicated on the companion curve, and the broken line is the calculated value for either. This figure shows that the calculation from the properties of single salt solutions is not only more useful than the assumption of proportionality, but that it is also more accurate. Yet interpolation from concentrated to dilute solutions with the assumption of proportionality would not lead to serious errors even in the worst cases. The deviation of the measured values from those calculated from the properties of single salt solution varies widely from salt to salt, but in no case is the difference more than a few per cent, even in molal solutions.

This paper includes two quite different subjects: the calculation of the equilibrium properties of solutions of simple ions from the physical properties of the ions, and the calculation of the properties of mixed solutions from those of solutions of the single salts. There is one objective common to both treatments, — to show that much may be, and already has been, accomplished in the treatment of concentrated solutions. The extension of the first treatment to more complicated ions may be left to the specialists, but the application of the second method may be made with profit in any study of the physical or chemical equilibria involving electrolyte solutions. It is not necessary that the method used be the same in all its details as that outlined here, but it is important that we realize that a fairly simple and fairly accurate approximate treatment is possible. The

uncertainties do increase with increasing concentration, but not very rapidly. A little further systematic work should reduce the uncertainties, but even now our methods of handling the results are as good as all but the best experimental work.

REFERENCES

- (1) ÅKERLÖF, G., AND THOMAS, H. C.: J. Am. Chem. Soc. **56**, 593 (1934).
- (2) ÅKERLÖF, G.: J. Am. Chem. Soc. **56**, 1439 (1934).
- (3) ÅKERLÖF, G., AND TURCK, H. E.: J. Am. Chem. Soc. **56**, 1875 (1934).
- (4) BRØNSTED, J. N.: J. Am. Chem. Soc. **44**, 877 (1922).
- (5) BRØNSTED, J. N.: J. Am. Chem. Soc. **45**, 2898 (1923).
- (6) BJERRUM, N.: Kgl. Danske Videnskab. Selskab Math-fys. Medd. **1**, No. 9 (1926).
- (7) DEBYE, P., AND HÜCKEL, E.: Physik. Z. **24**, 185 (1923).
- (8) DEBYE, P., AND McAULAY, J.: Physik. Z. **26**, 22 (1925).
- (9) DEBYE, P.: Z. physik. Chem. **130**, 56 (1927).
- (10) DEBYE, P., AND FALKENHAGEN, H.: Physik. Z. **29**, 121, 401 (1928).
- (11) FAJANS, K., AND KARAGUNIS, G.: Z. angew. Chem. **43**, 1046 (1930).
- (12) GRONWALL, T. H., LAMER, V. K., AND SANDVED, K.: Physik. Z. **29**, 358 (1928).
- (13) GUGGENHEIM, E. A.: Phil. Mag. [7] **19**, 588 (1935).
- (14) HALL, R. E., AND HARKINS, W. D.: J. Am. Chem. Soc. **38**, 2658 (1916).
- (15) HARNED, H. S.: J. Am. Chem. Soc. **48**, 326 (1926).
- (16) HARNED, H. S., AND ÅKERLÖF, G.: Physik. Z. **27**, 411 (1926).
- (17) HARNED, H. S.: in H. S. Taylor's *Treatise on Physical Chemistry*, 2nd Edition, Vol. I, p. 803. D. Van Nostrand Co., New York (1931).
- (18) HAUSRATH, H.: Ann. Physik [4] **9**, 522 (1902).
- (19) HÜCKEL, E.: Physik. Z. **26**, 93 (1925).
- (20) LANNUNG, A.: Z. physik. Chem. **170A**, 134 (1934).
- (21) ONSAGER, L.: J. Am. Chem. Soc. **58**, 1486 (1936).
- (22) PAULING, L. J.: J. Am. Chem. Soc. **50**, 1036 (1928).
- (23) ROBINSON, R. A., AND SINCLAIR, D. A.: J. Am. Chem. Soc. **56**, 1830 (1934).
- (24) ROBINSON, R. A.: J. Am. Chem. Soc. **57**, 1161 (1935).
- (25) ROBINSON, R. A.: J. Am. Chem. Soc. **57**, 1165 (1935).
- (26) ROBINSON, R. A., AND JONES, R. S.: J. Am. Chem. Soc. **58**, 959 (1936).
- (27) ROBINSON, R. A.: Personal communication.
- (28) SCATCHARD, G.: Chem. Rev. **8**, 321 (1931).
- (29) SCATCHARD, G.: Physik. Z. **33**, 22 (1932).
- (30) SCATCHARD, G., AND PRENTISS, S. S.: J. Am. Chem. Soc. **54**, 2690 (1932).
- (31) SCATCHARD, G., AND PRENTISS, S. S.: J. Am. Chem. Soc. **55**, 4355 (1933).
- (32) SCATCHARD, G., AND PRENTISS, S. S.: J. Am. Chem. Soc. **56**, 807 (1934).
- (33) SCATCHARD, G., AND PRENTISS, S. S.: J. Am. Chem. Soc. **56**, 1486 (1934).
- (34) SCATCHARD, G., AND PRENTISS, S. S.: J. Am. Chem. Soc. **56**, 2314 (1934).
- (35) SCATCHARD, G., AND PRENTISS, S. S.: J. Am. Chem. Soc. **56**, 2320 (1934).
- (36) SCATCHARD, G., AND BENEDICT, M. A.: J. Am. Chem. Soc. **58**, 837 (1936).
- (37) SCATCHARD, G., HAMER, W. J., AND WOOD, S. E.: Unpublished.
- (38) WIEN, M.: Ann. Physik [4] **83**, 327 (1927).
- (39) WIEN, M.: Ann. Physik [4] **85**, 795 (1928).
- (40) WYMAN, J., JR.: J. Am. Chem. Soc. **58**, 1482 (1936).

THE DIELECTRIC CONSTANTS OF SOLIDS AND MOLECULAR ROTATION

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INTRODUCTION

In recent years the dielectric constants of solids have received much less attention from scientific investigators than have those of liquids, which have given such valuable information concerning molecular structure. However, there is much of interest to be found in measurements of the dielectric constant of solids, particularly of solids with rotating molecules which will form the subject of a major part of the present discussion.

The dielectric constant of a substance was originally represented as arising from the induction of charges on the surfaces of the molecules (61, 10), the molar polarization P of the substance being given by the expression

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4\pi N}{3} \alpha_0$$

in which ϵ is the dielectric constant, M the molecular weight, d the density, N the number of molecules in a mole, and α_0 the dipole moment per molecule resulting from shift of charge induced by an electric field of unit intensity. The Maxwell relation (57) $\epsilon = n^2$, where n is the index of refraction, leads to identity between the molar polarization and the molar refraction. Substances for which the polarization is nearly equal to the molar refraction for visible light show an approximately constant polarization as required by the Clausius-Mosotti relation and, consequently, a dielectric constant which decreases slightly with rising temperature as the density decreases. Debye (19) accounted for the many substances which did not obey this relation by introducing the additional term

$$P_M = \frac{4\pi N}{3} \frac{\mu^2}{3kT}$$

in which μ is the permanent dipole moment of the molecule, k the Boltzmann gas constant, and T the absolute temperature. The entire expression may be written

$$P = a + b/T$$

Many determinations of the induced polarization a have shown it to be always larger, usually only slightly (76), than the molar refraction, which arises from the displacement of the electrons within each molecule and may, therefore, be represented as P_E . As this difference arises from the displacement of nuclei, atoms, or groups, which have too great inertia to be displaced in the rapidly alternating electric field of the light wave used in determining the electronic polarization P_E , it is called the atomic polarization P_A . $P_M = b/T$ may be much larger than $P_E + P_A = a$, but is, of course, zero when the molecules have no permanent dipole moments and will also be zero when the molecular dipoles are unable to orient in an externally applied field. The dielectric constant, therefore, gives us a means of examining not only the distribution and mobility of charge inside the molecule but also the freedom of the molecule in its environment.

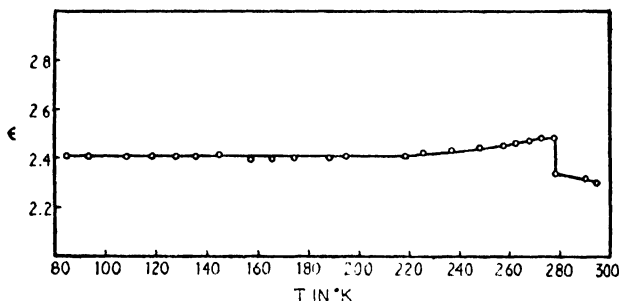


Fig. 1. Dielectric constant-temperature curve (at 50 kilocycles) of benzene

The experimental values for the dielectric constants of solids are less accurate than those for liquids, because of the difficulty of completely filling the space between the plates of the condenser with a homogeneous sample. The presence of impurities, particularly ionic impurities, even in extremely small quantities may introduce considerable errors in the neighborhood of the melting point. This latter effect necessitates caution in some cases in the interpretation of results near the melting point, but, in general, the validity of the conclusions to be drawn is not affected by the experimental errors.

NON-POLAR MOLECULES

For a solid consisting of non-polar molecules, that is, of molecules with no permanent dipole moment, the dielectric constant is very close to the square of the refractive index for visible light, and differs from the dielectric constant of the liquid only because of the difference in the number of molecules in unit volume. Thus, in the case of the non-polar substance ben-

zene n_D^2 for the liquid at 20°C. is 2.25 and ϵ is 2.29 (84), while at 5°C. the dielectric constant of the supercooled liquid is 2.34 (78) and that of the solid 2.46. The failure of the dielectric constant-temperature curves for such solids (figure 1) to show any rise with increasing density at low temperatures is due to the fact that the material is usually frozen between the fixed plates of a condenser, so that increasing density does not alter the amount of material between the plates. The total polarization P is 27.01 for the vapor (58), 25.62 for the liquid at 10°C. (84), and 26.70 for the solid at 5°C. according to Errera (23), and 28.5 at 0°C. according to Morgan and Lowry (60). As P_E is 25.1, P_A may be taken as 1.9 (58). The difference in polarization between the solid and the liquid is evidently within the experimental error, as would be expected in view of the practically negligible effect which the environment of a group has upon its polarizability (75, 77). The case of benzene is typical of a large class of substances without dipole moment, such as the paraffins, whose dielectric constants depend upon the induced displacement of electrons and, to a very small extent, of atoms or groups in the molecules. These dielectric constants are almost independent of physical state and temperature, except in so far as these factors determine the number of molecules in unit volume, or, in other words, the number of charges present to undergo displacement. The slight rise of the curve for benzene near the melting point is the effect of minute traces of impurities.

NON-METALLIC IONIC SOLIDS

In non-metallie ionic solids, the dielectric constant still arises only from shift of charge as in the non-polar molecular solids, but the shift of ionic charge, which gives rise to P_A , may play a more important part than the electronic shift. Table 1 gives for the cubic latticed and, therefore, isotropic alkali metal halides except those of cesium the values of the dielectric constant ϵ and the squares of the refractive indices n_0^2 extrapolated from the visible region to infinite wave length by means of a classical dispersion formula, and table 2 gives the total and the atomic polarizations calculated from these values (24). The considerable differences between n_0^2 and ϵ are due to the displacements of the ions in the lattices. Both the total polarization P and the electronic P_E ($= P - P_A$) increase with increase in the size of either ion. The same trend is evident in the values of P_A , but it is only approximate. The larger one ion is, the smaller is the effect of the size of the other ion upon P_A . For ordinary field strengths, the actual ionic displacement is very small. For example, calculation shows that the average displacement of each ion in rubidium iodide produced by 300 volts per centimeter is only 10^{-6} A.U. As the displacement of the ions in the externally applied field depends upon the interionic forces, Errera

(24) has applied the Born theory of the lattice (6) to these dielectric constant values to calculate the infra-red wave lengths corresponding to the characteristic vibration frequencies in the lattices. From consideration of the fraction of the dielectric constant which is due to ionic displacement expressed as $(\epsilon - n_0^2)/(\epsilon - 1)$, Errera and Brasseur (26) conclude that, for solids of one family, the fraction of the total polarization dependent upon ionic displacement is greater, the smaller the ionic radius, the smaller the inter-ionic distances, and the smaller the electronic polarizability. At first glance, this statement appears to be a direct contradiction of the evidence given by the P_A values in table 2 which tend to increase with ionic size.

TABLE 1

Dielectric constants and squares of refractive indices of alkali metal halides

	F		Cl		Br		I	
	ϵ	n_0^2	ϵ	n_0^2	ϵ	n_0^2	ϵ	n_0^2
Li.....	9.2	1.91	11.05	2.68	12.1	3.04	11.03	3.55
Na.....	4.9	1.74	5.77	2.32	5.99	2.60	6.60	2.96
K.....	6.05	1.83	4.76	2.17	4.78	2.35	4.94	2.64
Rb.....	5.91	1.93	5.20	2.18	4.70	2.34	4.81	2.58

TABLE 2

Total and atomic polarizations of alkali metal halides

	F		Cl		Br		I	
	P	P_A	P	P_A	P	P_A	P	P_A
Li.....	7.20	4.90	15.80	8.44	19.74	9.60	25.38	10.24
Na.....	8.45	5.48	16.58	8.30	20.05	8.90	26.60	10.44
K.....	14.63	9.57	20.83	10.29	25.10	11.65	30.18	11.45
Rb.....	17.32	10.73	25.21	13.02	27.25	12.06	33.41	12.82

Increasing ionic size and separation lessen the binding forces between ions of opposite charge and, therefore, cause increasing P_A . The conclusion of Errera and Brasseur is based upon the effect per cm.³ of substance, while the polarization values are based upon the number of molecules per mole. The greater number of ionic charges present per cm.³ in the substances formed of small ions more than compensates for the stronger binding forces and thus gives higher dielectric constants.

In anisotropic solids, the different forces in different directions cause differences in the dielectric constants in these directions. Thus, in the orthorhombic sulfates of strontium, barium, and lead—celestite, barite,

and anglesite (26)—the refractive index of each is about the same along its three crystal axes, but the dielectric constant along the *b*-axis is approximately double those along the *a*- and *c*-axes, which are nearly equal. ϵ_0 for anglesite has the unusually high value 54.6, more than ten times that due to electronic displacement alone. In a group of six rhombohedral carbonates, the refractive index along the equal *a*- and *b*-axes is larger than that along the *c*-axis. The dielectric constant along the *a*- and *b*-axes is slightly larger than that along the *c*-axis except in magnesite, where it is 15 per cent smaller than that along the *c*-axis. A group of four orthorhombic carbonates has almost equal refractive indices along the *a*- and *b*-axes, with somewhat lower values along the *c*-axis. The same is approximately true of the dielectric constants except in aragonite, which has a value along the *a*-axis 60 per cent higher than that along the *b*-axis. Titanium dioxide (71, 56) in the form of brown rutile, which is tetragonal, is a particularly striking example of the effect of ionic displacement, having a dielectric constant 170 parallel to its optic axis and a value 86 perpendicular to this axis. The excess of the mean values over the mean dielectric constant 78 found for transparent rutile may be due to impurities.

Rising temperature tends to decrease the dielectric constant of a non-metallic ionic solid by decreasing the number of molecules per cm.³ as in the case of the non-polar molecular solids. At the same time, however, the greater separation of the ions produced by the increasing volume weakens the forces between them and thus increases their ease of displacement. In the cases of calcium fluoride and sodium chloride examined by Bretscher (7), the calculated increase of dielectric constant due to weakening of the interionic forces is nearly three times as large as the decrease caused by decreasing density. The expression for the total variation of dielectric constant with temperature obtained by Bretscher is

$$\frac{1}{\epsilon} \frac{d\epsilon}{dT} = \left\{ \frac{(\epsilon - \epsilon_0)}{3\epsilon} (n + 2) - \frac{\epsilon - \epsilon_0}{\epsilon} - \frac{(\epsilon_0 - 1)(\epsilon_0 + 2)}{3\epsilon} \right\} \frac{1}{V} \frac{\partial V}{\partial T}$$

where *V* is the volume and ϵ_0 is the contribution to the dielectric constant of all oscillators except that due to residual rays. The values calculated by Bretscher for the temperature variation of ϵ are considerably smaller than the observed, but of the correct order of magnitude.

NON-ROTATING POLAR MOLECULES

Solids consisting of polar molecules, that is, molecules possessing permanent dipole moments, commonly behave like those consisting of non-polar molecules, because solidification usually fixes the molecules with such rigidity in the lattice that orientation of the dipoles in an externally applied field is impossible. P_M is therefore zero, and the dielectric con-

stant depends simply upon the displacement of charges induced inside the molecule. The values of the electronic polarization P_E are unaffected by the presence of the dipole moments and the values of P_A are little, if any, larger than those of the non-polar molecules (76). The dielectric constant of the solid thus depends upon the same factors as in the non-polar molecular solid. The dielectric constant temperature curve shows a great difference at the melting point, for, in the case of the non-polar molecular solid, the small change produced by melting is usually a slight drop caused by decrease in the number of molecules per cm.³, while the polar molecules

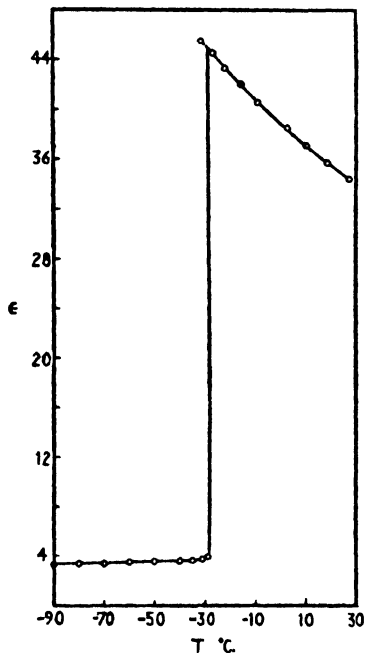


FIG. 2. Dielectric constant-temperature curve (at 70 kilocycles) of nitromethane

acquire freedom of rotation on melting and P_M changes abruptly from zero to a value often many times that of $P_E + P_A$. Nitromethane (85), which has a large dipole moment and, consequently, a large value of P_M in the liquid, affords a particularly striking example of this change at the melting point (figure 2). An impure sample of a polar substance may show a considerable increase in dielectric constant and in apparent conductance as the melting point is approached, presumably because of the separation of a small amount of a liquid phase. A slight increase in carefully purified solids may be due to the acquisition by an occasional molecule of sufficient

freedom to orient in an externally applied field or to the effect of increasing conductance upon the apparent value of the dielectric constant. A carefully purified solid nitrobenzene of melting point 5.67°C . showed an increase in dielectric constant from 3.25 at 0°C . to 3.62 at 5°C ., while pure solid benzene of melting point 5.4°C . increased by only 0.009 from 0° to 5°C ., and benzene saturated with water (0.01 to 0.05 per cent) before freezing increased by only 0.01 from 0° to 5°C . (78). These comparative figures would certainly be interpreted as giving evidence of some molecular rotation in the solid nitrobenzene were it not that a very minute amount of ionic impurity could conceivably have caused the rise in dielectric constant as the melting point was approached. It seems probable, however, that loosening of the molecular lattice as the melting point is approached gives sufficient freedom to an occasional molecule to permit its orientation in the externally applied field.

MOLECULAR ROTATION AND THERMAL ENERGY

In considering the possibility of molecular rotation in solids it is necessary to weigh also the evidence given by specific heats and x-ray analysis. The thermal energy of solids as evidenced by their specific heats is due mainly to the translational vibrations of the atoms, ions, or molecules about fixed points in the crystals or in the molecules, although rotational vibration or very occasionally, free rotation of a molecule or polyatomic ion may play a part. A molecule in which all the atoms lie in a straight line may rotate easily around this line as axis, but, as such rotation involves only the minute inertia of the electrons, it has a negligible effect on the ordinary properties of the substance and will not be considered here. Molecular rotation as discussed in the present paper means rotation in which an actual translation of atomic nuclei occurs. Recent work on the diffraction of x-rays by liquids (68) has indicated the existence of a rough approximation to a lattice-like arrangement of molecules, as in crystals. Instead of the perfectly random translational motion and complete freedom of rotation which was formerly attributed to the molecules of a liquid, Debye has recently suggested (21) that the molecules are vibrating about points which themselves move relatively slowly through the liquid. Each molecule is, of course, acted upon by strong electric forces due to the surrounding molecules. Unless the molecule has spherical symmetry, one or more of its orientations in the electric field of force surrounding it are more stable than any others. If the maximum difference of potential energy between the different orientations of the molecule is less than its thermal rotational energy, the molecule can rotate freely, but if this energy difference is greater than the thermal energy of the molecule, the latter

will tend to oscillate rotationally about an orientation of minimum potential energy.

The problem of rotational oscillation, which has been treated theoretically by Pauling (66) and others (31, 32) for crystals, may be simply illustrated by considering the case of the hydrogen chloride molecule in its crystal. Since this molecule contains a dipole in the H—Cl line with its positive end toward the hydrogen, it will tend to orient with this H—Cl axis in the direction of the electric field in which the molecule lies, the positive hydrogen side of the molecule pointing toward the negative side of the field. Turning of the axis of the molecule through an angle θ from this position will increase the potential energy of the molecule by an amount V , which may be conveniently represented as a function of θ by the equation

$$V = V_0 (1 - \cos \theta)$$

$2V_0$ is evidently the increase in potential energy when the axis of the molecule is turned through an angle of 180° . The thermal energy of the molecule will cause it to rotate back and forth around the position $\theta = 0^\circ$, unless this thermal energy is greater than $2V_0$, when it will turn over the potential energy hump and rotate freely. Pauling (66) gave an approximate theoretical treatment of the problem, showing that the commencement of molecular rotation with rising temperature accounted for a number of transitions which specific heat measurements had revealed in certain solids, and predicting that dielectric constant measurements would show freedom of rotation above these transitions. Fowler (31) recently used partition functions to represent the effect of molecular rotation upon the specific heats and dielectric constants of these substances which show transitions. The equations thus obtained show that the transitions should occur, but require the changes to be more gradual than those actually observed and are not successful in predicting where they should occur. Frenkel, Todes, and Ismailow (32) have based an approximate treatment on the assumption that the transition from non-rotation to rotation is very sharp, so that a rotating phase and a non-rotating phase are in equilibrium at a definite transition temperature. They are unable, however, to obtain much support of their treatment from the experimental facts. In view of the difficulty of fitting any quantitative theoretical treatment to the facts, it seems desirable to assemble a large body of experimental evidence and consider it qualitatively in the light of the fundamental principles which must guide any quantitative treatment.

As the specific heat depends upon the energy associated with the various

oscillations in the crystal, its variation with temperature may give evidence as to oscillation or free rotation of the molecule. The rotational oscillation of the molecules increases with rising temperature and may acquire sufficient energy in the solid to pass over the hump in the potential energy curve, which means free rotation. Although one would expect this attainment by the molecules of sufficient energy to rotate to be distributed over a considerable interval of temperature, it should be remembered that the setting-in of rotation of one molecule will weaken the forces which it exerts upon its neighbors and thereby facilitate their rotation. The setting-in of rotation may, therefore, be sharp like melting, and should commonly cause structural changes in the solid. The resulting transition is shown by a break in the specific heat-temperature curve, which rises sharply because of the heat of transition and sinks sharply again. However, such a break may also accompany a transition which can have nothing directly to do with molecular rotation.

As rotation makes the field of force exerted by a molecule symmetrical around the axis of rotation, it is apt to give symmetry to a lattice. If the rotating molecule is fairly symmetrical in form, the lattice is usually one which could be formed of close-packed spheres, commonly cubic or hexagonal. From the opposite point of view, if the crystal is isotropic, the potential energy of a molecule will tend to vary less with its orientation in the lattice, which means that the molecule is more apt to rotate freely. It is obviously desirable to correlate the lattice structure as revealed by x-ray analysis with the evidence of molecular rotation.

SUMMARY OF EXPERIMENTAL MATERIAL

Table 3 summarizes the information in regard to rotation or non-rotation in a large number of solids which either show rotation or might be expected to show it but do not. The table aims at completeness as far as concerns the information given by dielectric constant measurements, which provide the best means of examining the rotation of a molecule having a dipole moment, and lists most of the transitions more or less clearly indicated by specific heat measurements as due to the commencement or the cessation of rotation, but does not include all of the cases in which symmetry deduced from x-ray analysis is attributed to rotation. The first column gives the molecule or ion under consideration, and the third gives the temperatures of the rotational transitions and other transitions in the neighborhood or a statement of the absence of rotation. The second and fourth columns give, when possible, the forms of lattice below and above the transitions. Where no rotation occurs below a transition given in the third column, no statement of the fact is made in the second column.

TABLE 3
Lattice form and rotation or non-rotation of molecules in solids

MOLECULE OR ION	REFERENCES	LATTICE BELOW TRANSITION*	TEMPERATURE OF TRANSITION, °K.	LATTICE ABOVE TRANSITION*
H_2	(66)	Rotates at very low temperature		Hexagonal
Cl_2	(30)	No rotation		
Br_2	(55)	No rotation		
I_2	(66, 33)	Orthorhombic. No rotation		
O_2	(28, 35, 11, 69)	Orthorhombic	23 8	Orthorhombic
		Orthorhombic	43 5	Rotation. Hexagonal
N_2	(28, 11, 69, 47)	Cubic	35 4	Rotation. Hexagonal
CO	(28, 11)	Cubic	61 5	Rotation. Hexagonal
NO	(30, 45)	No rotation indicated		
N_2O	(14, 29)	Cubic. No rotation		
CO_2	(28, 29)	Cubic. No rotation		
CH_4	(11, 15)	Cubic	20 4	Rotation. Cubic
SiH_4	(12)	Cubic. No evidence of rotation	63 4	Rotation. Higher symmetry
NH_3	(30, 14, 79)			
PH_3	(13)	Rotation	30	Rotation
			89	Rotation. Cubic (103°)
AsH_3	(83)	Rotation. Cubic	20-32 1	Rotation. Cubic (103°)
			106 6	Rotation
NH_4^+ (in NH_4F)	(74)		242 4	No rotation indicated
				Hexagonal

NH_4^+ (in NH_4Cl)	(72, 74, 8)	Rotation. Cubic (CsCl type)	242.7	Rotation. Cubic (CsCl type)
		Rotation. Cubic (NaCl type)	457.4	
NH_4^+ (in NH_4Br)	(74, 8)	Tetragonal	235.1	Rotation. Cubic (CsCl type)
		Rotation. Cubic (CsCl type)	410.9	Rotation. Cubic (NaCl type)
NH_4^+ (in NH_4I)	(74, 8)	Rotation. Cubic (CsCl type)	230.6	Rotation. Cubic (CsCl type)
			260.6	Rotation. Cubic (NaCl type)
$\text{C}_6\text{H}_{11}\text{NH}_3^+$ (in $\text{NH}_4\text{C}_6\text{H}_{11}\text{Cl}$)	(86)	Tetragonal	221.5	
			246.5	Limited rotation. Tetragonal, smaller unit cell
$\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$	(2)	Orthorhombic. No rotation		
		Hexagonal	213	NH_4^+ rotating. Hexagonal
		NH_4^+ rotating. Hexagonal	255	NH_4^+ rotating. Orthorhombic
		NH_4^+ rotating. Orthorhombic	305	NH_4^+ rotating. Orthorhombic
		NH_4^+ rotating. Orthorhombic	357	NH_4^+ rotating. NO_3^- probably rotating about the normal to the plane of the oxygens.
NH_4NO_3	(53, 41)			Tetragonal
			398	Both ions rotating freely. Cubic
NO_3^- (in NaNO_3)	(51, 54, 5)	Hexagonal	548	Rotation of NO_3^- about the normal to the plane of the oxygens gradually attained. Hexagonal

* Unless otherwise indicated this information is taken from the compilations by R. W. G. Wyckoff, *The Structure of Crystals*, 2nd edition (The Chemical Catalog Co., Inc., New York, 1931) and *Supplement for 1930-1934 to the Second Edition* (The Chemical Catalog Co., Inc., New York, 1935).

TABLE 3—Continued

MOLECULE OR ION	REFERENCES	LATTICE BELOW TRANSITION*	TEMPERATURE OF TRANSITION, °K.	LATTICE ABOVE TRANSITION*
NO_2^- (in KNO_3)	(52)	Orthorhombic	400.8	NO_2^- rotating about the normal to the plane of the oxygens. Hexagonal
PH_4I	(17)	Tetragonal. No rotation		
H_2O	(78, 63)	Hexagonal. Rotation with difficulty		
H_2O (in $\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$)	(26, 27)	Tetragonal. Rotation with some difficulty		
H_2O (in $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$)	(26)	Orthorhombic. Rotation not evidenced		
H_2O (in $\text{SrPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$)	(26)	Monoclinic. Rotation not evidenced		
H_2O (in $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$)	(26)	Monoclinic. Rotation not evidenced		
H_2O (in $\text{Y}_2\text{Pt}_2(\text{CN})_{12} \cdot 21\text{H}_2\text{O}$)	(27)	Orthorhombic. Rotation with some difficulty		
H_2O (in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	(26)	Triclinic. Rotation with some difficulty		
H_2O (in $\text{Na}_2\text{S}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$)	(26)	Monoclinic. Rotation with some difficulty		
H_2O (in $\text{NaKC}_2\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$)	(50, 25, 93)	Rotation. Orthorhombic		
H_2S	(79, 13, 49)	Rotation. Cubic	103.5 126.3	Rotation. Cubic Rotation
H_2Se	(83)	No rotation	<89	Rotation. Cubic (103°)
HF	(14, 13)	Orthorhombic	98.9	Cubic. Rotation
HCl	(30, 16, 80, 37)			

		Orthorhombic Cubic. Rotation Cubic. Rotation	89 113 117	Cubic. Rotation Cubic. Rotation Cubic. Rotation
HBr.....	{ 30, 80, 38, 70, 64)	Tetragonal (face-centered)		Tetragonal (face-centered). Rotation
HI.....	{ (30, 80, 39)	Rotation Tetragonal (face-centered)	70	Tetragonal (face-centered). Rotation
HCN.....	(83)	No rotation		
CN ⁻ (in KCN).....	(90)	Probably rotating. Cubic		
CH ₃ Cl.....		No rotation around axis perpendicular to axis of symmetry	126	Tetragonal (face-centered). Rotation
CH ₃ Br.....		No rotation around axis perpendicular to axis of symmetry		
CH ₃ I.....		No rotation around axis perpendicular to axis of symmetry		
CH ₃ Cl ₃		No rotation around axis perpendicular to axis of symmetry		
CHCl ₃		No rotation around axis perpendicular to axis of symmetry		
CH ₃ NO ₂	(85)	No rotation around axis perpendicular to axis of symmetry		
CH ₃ Cl (CH ₂ Cl).....	(79)	No rotation around axis perpendicular to axis of symmetry		
n-C ₂ H ₅ Br.....	(46)	No rotation		

TABLE 3—*Concluded*

MOLECULE OR ION	REFERENCES	LATTICE BELOW TRANSITION*	TEMPERATURE OF TRANSITION, °K.	LATTICE ABOVE TRANSITION*
CH ₃ OH.....	(65, 48, 79, 82)	No rotation	159	Limited rotation
(CH ₃) ₂ COH.....	(82)	No rotation		
<i>n</i> -C ₃ H ₇ OH.....	(82)	No rotation. Monoclinic	289	Rotation around chain axis. Hexagonal
<i>n</i> -C ₁₂ H ₂₅ OH.....	(2)	No rotation	316	Limited rotation
C ₁₁ H ₂₃ CO ₂ C ₂ H ₅	(9)	No rotation	203	Partial rotation
(CH ₃) ₂ SO ₄	(78)	No rotation		
(C ₂ H ₅) ₂ SO ₄	(78)	No rotation		
<i>d</i> -Camphor.....	(92, 88)	Hexagonal (rhombohedral)	233-236	Rotation. Hexagonal (rhombohedral)
		Rotation. Hexagonal (rhombohedral)	370	Rotation. Cubic
<i>dl</i> -Camphor.....	(92, 88)		125-208	Rotation
Borneol.....	(92, 88)	Partial rotation	173-223 343-348	Partial rotation Rotation
Isoborneol.....	(92, 88)	Partial rotation	173-223 285-319	Partial rotation Rotation
Bornyl chloride.....	(92)		130-165	Rotation
<i>d</i> -Camphoric anhydride.....	(92)		408	Rotation
C ₆ H ₁₁ OH.....	(88)		205-230	Rotation
C ₆ H ₅ OH.....	(46)	No rotation		
(C ₂ H ₅) ₂ O.....	(59)	No rotation		

$C_6H_5OCH_3$	(46)	No rotation	
$CH_3OC_6H_4OCH_3$	(46)	No rotation	
$(CH_3)_2CO$	(59)	No rotation	
$C_6H_5COC_6H_5$	(59)	No rotation	
$C_6H_5NO_2$	(78)	No rotation	
$C_6H_5NH_2$	(78)	No rotation	
CH_3NH_2	(59)	No rotation	
$(CH_3)_2(COOH)_2$	(88)	No rotation	

DISCUSSION OF EXPERIMENTAL MATERIAL

In solid hydrogen, which crystallizes in the hexagonal system corresponding to the closest possible packing of spheres, the H_2 molecule rotates (66). The forces between the hydrogen molecules are so weak that there is little variation in the energy of their orientation, and they rotate even with the low energies which they possess a few degrees above the absolute zero. On the other hand, the equally symmetrical diatomic molecule of iodine shows no rotation in its orthorhombic lattice, because the spacing of the molecules is so close in this lattice that they have no room to turn over. The specific heat curves for solid chlorine and bromine, the crystal structures of which are unlisted, also give no evidence of rotation. The upper of the two transitions listed for oxygen is indicated by the specific heat curve as due to the setting in of rotation or, at least, to a great increase in any freedom of rotation possibly existing below it and above the lower transition. The rotation of the nitrogen molecule sets in at a slightly lower temperature, while that of the less symmetrical carbon monoxide molecule, which has a small dipole moment, 0.11×10^{-18} , requires an appreciably higher temperature. One would expect to find rotation setting in for nitric oxide at a temperature not far from that of the rotational transition in carbon monoxide, but specific heat measurements give no positive evidence of any transition. If the molecules form the complex N_2O_2 at low temperatures, of which there is indication (45), the absence of rotation is explained. The linear triatomic molecules of nitrous oxide and carbon dioxide show no rotation in their cubic lattices because there is not sufficient space for end-over-end rotation.

Methane crystallizes in a cubic lattice and undergoes a sharp transition at $20.4^\circ\text{K}.$ as shown by the specific heat-temperature curve, without any apparent change in the lattice structure. The molecule has the form of a regular tetrahedron with rounded corners and an indentation in the middle of each edge. Its symmetry is such that there should be little variation in the energy of its orientation. Rotation can thus set in at the low temperature found for its transition. The corresponding silicon compound SiH_4 undergoes a less sharp transition at $63.4^\circ\text{K}.$ with a change to a more symmetrical lattice above the transition (12); data on the crystal structure are lacking. Although this monosilane molecule should be similar in form to that of methane, the larger silicon atom, which has a bond radius 50 per cent larger than that of carbon, gives a longer edge to the tetrahedron and a greater variation in the energy of molecular orientation, requiring a higher temperature to produce rotation.

The ammonia molecule, a flattened tetrahedron with a dipole moment of 1.46×10^{-18} (18), crystallizes in the cubic system. Neither specific heat nor dielectric constant measurements show molecular rotation in the

crystal. The considerable dipole moment of the molecule as well as the lower symmetry of its form causes a much greater variation in the potential energy of its orientation than that found in methane and monosilane, the energy differences being apparently greater than the thermal energy of rotational oscillation which the molecules acquire before melting. It would seem that rotation might occur fairly easily around the axis of the dipole moment, which is the perpendicular drawn from the nitrogen nucleus at the apex of the molecular pyramid to the triangular base at the three corners of which lie the hydrogen nuclei. This rotation would not be revealed by the dielectric constant measurements, as it involves no motion of the molecular dipole, but it has not been evidenced in the specific heat measurements.

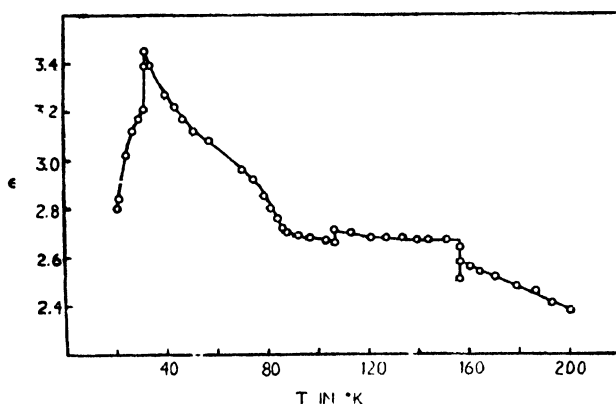


Fig. 3. Temperature dependence of the dielectric constant (at 50 kilocycles) of arsine

Phosphine, which should resemble ammonia in molecular shape as monosilane does methane, has a dipole moment of 0.55×10^{-18} and exists in a cubic lattice at 103°K. Below this temperature, two or more transitions are shown by the specific heats (13), which are indicative of molecular rotation above them. The small size of the dipole moment as compared to that of ammonia tends to reduce its contribution to the potential hump to slightly more than a third of that given by the ammonia dipole; the larger size of the molecule reduces the internal field and thus further reduces the potential hump which tends to prevent molecular rotation. However, the specific heat measurements show that the situation in phosphine is very involved, requiring further investigation. The dielectric constant of arsine (83) (figure 3) is higher at 20.5°K. than that of the liquid, but rises rapidly with temperature up to 32.1°K., where the rotational transition is complete. From this point up, the dielectric constant behaves like that

of a liquid, the lattice being reported cubic at 103°K. The second transition at 106.6°K. produces a very slight rise in the dielectric constant, which then falls off much more slowly than before. This is similar to the effect of the upper transition in hydrogen bromide, hydrogen iodide, and hydrogen sulfide, indicating, probably, a change in lattice dimensions with consequent change in internal field but no fundamental alteration in lattice structure.

The ammonium ion has a higher symmetry than the NH_3 molecule, presumably, resembling the methane molecule in form and size. However, because of its charge and that of the anion occurring with it in the solid ammonium halides, a much stronger internal field should exist in the crystal, and the differences in the energy of orientation should be greater than in the methane crystal. Accordingly, the rotational transition shown by specific heat measurements in ammonium chloride occurs at a temperature 222°C. above that in methane. The same transition is found in ammonium bromide and iodide, but the transition temperature becomes lower with increase in size of the halide ion, which weakens the internal field of the crystal, thus lowering the potential energy humps that tend to prevent rotation. Ammonium bromide has a tetragonal lattice below the transition and a cubic above, where rotation causes greater symmetry. The chloride and iodide have apparently not been investigated with x-rays below this transition. All three show a second transition, which seems to be a mere lattice change. Although the lattices are cubic both above and below these upper transition temperatures, they are of the sodium chloride type above and of the cesium chloride type below. In the ammonium fluoride crystal, which is hexagonal, the small fluoride ion gives so strong an internal field that molecular rotation is not indicated by the specific heat-temperature curve, although a slight hump occurs in it at about the temperature of the transition in ammonium chloride. Possibly a hydrogen bond between the ammonium and the fluoride ion may fix the former and prevent rotation.

n-Amylammonium chloride forms a lattice like that of the high temperature form of ammonium chloride, except that the extended zig-zag carbon chain extends the lattice in the direction of its axis, causing the form to be tetragonal. The separation of the chains is sufficient to permit rotation of the $\text{C}_5\text{H}_{11}\text{NH}_3^+$ ions around their axes, the rotation presumably setting in at the temperature of the lower transition. Molecular rotation accounts for the fact that ammonia is often found by x-ray analysis on axes of symmetry too high for its intrinsic symmetry, as in $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ (4). Bernal (2) by x-ray analysis has found $\text{C}_{18}\text{H}_{37}\text{NH}_3\text{Cl}$ to be orthorhombic without any rotation, but Müller (62) finds, with rising temperature, a gradual setting-in of rotation around the axis of the chain in the paraffins $\text{C}_{21}\text{H}_{44}$

and $C_{22}H_{48}$. The paraffins from $C_{24}H_{50}$ to $C_{34}H_{70}$ which he has investigated show transitions 5° to $10^{\circ}C.$ below their melting points with an apparent gradual setting-in of rotation in the narrow temperature ranges between the transition and the melting points.

Ammonium nitrate offers one of the most interesting examples of ionic rotation, although some doubt exists in regard to certain of the statements concerning it in table 3. A gradual transition at about $213^{\circ}K.$ suggests the setting-in of rotation of the ammonium ion, which is apparently occurring at $240^{\circ}K.$ The nitrate ion begins to rotate about the axis normal to the plane of its three oxygens when the transition from orthorhombic to tetragonal occurs at $357^{\circ}K.,$ and the cubic lattice results when this rotation becomes free in all directions at $398^{\circ}K.$ giving the nitrate as well as the ammonium ion spherical symmetry. Sodium nitrate shows a gradual transition at $548.5^{\circ}K.$ without change of crystal form, resembling the $357^{\circ}K.$ transition of ammonium nitrate in that the NO_3^- ion begins to rotate in the plane of its three oxygens, the number of rotating nitrate ions increasing rapidly as $548.5^{\circ}K.$ is approached. Austin and Pierce (1) have shown that, as the rotation increases, the crystal expands rapidly in the direction of the axes of rotation, indicating a weakening of the forces between the planes in which the ions lie. This type of rotation of the nitrate ion sets in at a considerably lower temperature in potassium nitrate, a lattice change within the orthorhombic system occurring. Kracek, Hendricks, and Posnjak (53) state the probability that the nitrate ion has spherical symmetry, owing to rotation, in calcium, barium, strontium, and lead nitrates and nickel nitrate hexammoniate. Many thermal transitions found in other inorganic solids containing small or symmetrical ions are doubtless caused by the setting-in of rotation, but the information concerning them is not sufficient to warrant their discussion here.

Phosphonium iodide, which has tetragonal symmetry, shows no transition between liquid air and room temperature (12), although one might look for molecular rotation. The lower symmetry of the lattice may make the potential humps high enough to prevent rotation. The transition in monosilane is $43^{\circ}C.$ higher than in methane, and in the strong field of the ionic lattice the difference between ammonium and phosphonium may be much greater.

For ice, which has a hexagonal lattice, the specific heat-temperature curve shows no transition at atmospheric pressure (73, 36) and gives no direct evidence of molecular rotation. The dielectric constant measurements (22, 40, 44, 63, 78, 89) show the possibility of rotation with a difficulty which increases rapidly but continuously with falling temperature. Under some conditions, the dielectric constant is distinctly higher than that of liquid water, 88.0 at $0^{\circ}C.$ (91), and its general behavior is like that

of a very viscous polar liquid, in which molecules with large dipole moments orient in an externally applied field but do so with great difficulty. For frequencies of 1/3 to 1/270 per second, Murphy (63) finds a value about 150 at $-90^{\circ}\text{C}.$, falling off gradually with rising temperature and rapidly with falling temperature. His values, about 99 for 1000 cycles at $0^{\circ}\text{C}.$, for example, are higher than those of Smyth and Hitchcock (78), which are reproduced in figure 4 because they cover such a range as to show well the decrease in dielectric constant with rising temperature at low frequencies like that in a polar liquid. The higher values found by Murphy may be

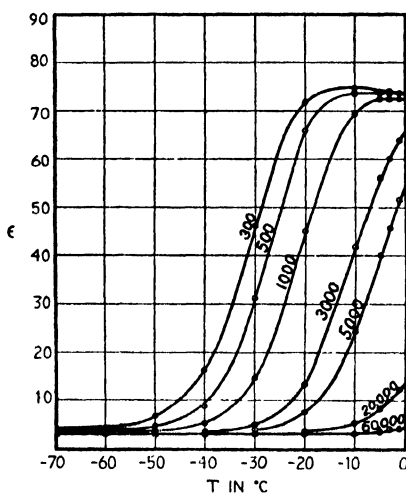


FIG. 4

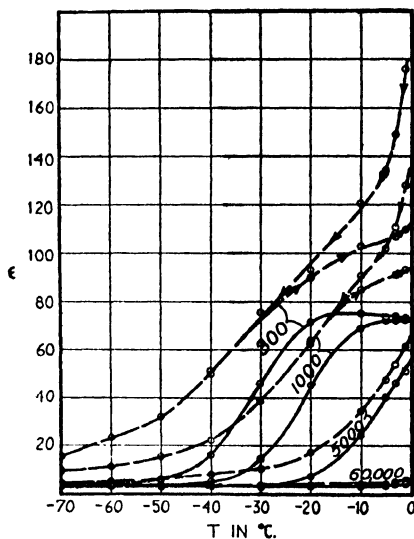


FIG. 5

FIG. 4. Variation of the dielectric constant of ice with temperature and frequency (in cycles).

FIG. 5. Variation of the dielectric constant of frozen 0.0002 *M* potassium chloride solution with temperature and frequency (in cycles).

due to better filling of his condenser with the solid or to ionic impurities, which are sufficient even in distilled water to raise the value appreciably (78).

Pauling (67) accounts for the entropy of ice by supposing that a crystal can exist in any one of a large number of configurations, each corresponding to certain orientations of the water molecules and change from one configuration to another resulting from rotation of some of the molecules or movement of some of the hydrogen nuclei to other equilibrium positions in the lattice. The very recent discussion of the specific heat and entropy of ice by Giaque and Stout (36) adopts this point of view in contrast to

the earlier view of Giauque and Ashley (34), which supposed rotation of the H_2O molecule even at very low temperature around the line bisecting the $\text{H}-\text{O}-\text{H}$ angle, a view difficult to reconcile with the strong internal field of the crystal and the consequent variation of potential energy with the orientation around this axis. Huggins (43) has given a qualitative explanation of the dielectric constant of ice, in terms only of the displacement of the hydrogen nuclei from one equilibrium position to another between the oxygens in the lattice. Stearn and Eyring (87) have calculated from the observed dielectric constant values that such displacements involve reasonable energy changes, as would molecular rotation also. Although the behavior of the dielectric constant of ice is explicable in terms of other types of polarization than that depending upon the orientation of its polar molecules, the turning of the molecule with difficulty in the externally applied field seems to be consistent with all the facts (cf. 20, 3). The fact that a similar dependence of dielectric constant upon frequency and temperature has been observed in four salts with water of hydration (26, 27), in two of them along one crystal axis only, supports the supposition that it is a question of molecular orientation or rotation in ice.

The great effect of ionic impurities upon the dielectric constant of ice is shown by figure 5, in which the solid lines represent the dielectric constants of frozen conductivity water and the broken lines the values for a frozen 0.0002 M solution of potassium chloride which contained 278,000 water molecules for each potassium ion and chloride ion (78). The curves for each frequency are connected by a bracket, which is marked with the frequency in cycles. At low frequencies the dielectric constants of the frozen solution were much higher on first cooling down slowly from the freezing point than on warming up. Arrows pointing downward and upward distinguish the curves for falling and rising temperatures. With increasing frequency, the difference between the falling temperature and the rising temperature curves becomes small and actually reverses, and the difference between the pure ice and the frozen solution almost disappears.

Errera and his coworkers (26, 27) have found that the dielectric behavior of a number of salt hydrates is very similar along at least one crystal axis to that of ice. Single crystals of $\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$ and $\text{Y}_2\text{Pt}_3(\text{CN})_{12} \cdot 21\text{H}_2\text{O}$ show dielectric constants along the a - and b -axes almost independent of temperature and frequency, while along the c -axis the dielectric constant is much higher and dependent upon temperature and frequency, indicating the rotation with some difficulty of one or more of the molecules of water of hydration. Rotation appears possible in the corresponding calcium and strontium compounds and in $\text{BaPt}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$, which has a dielectric constant of 9.5 along the c -axis. Rotation is also evident in the pentahydrates of copper sulfate and sodium thiosulfate.

The extraordinary behavior (50, 25, 93) of Rochelle salt, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot$

$4\text{H}_2\text{O}$, must be attributed to orientation of the H_2O dipoles. Dielectric constant values as high as 20,000 and as low as -381 have been observed, the values depending not only upon frequency and temperature but also upon field strength. The dielectric constant shows an anomalous dispersion curve similar in form to that given by a refractive index in a region of absorption. Orientation of the dipoles in the external field is accompanied by further orientation in the internal field, analogous to that occurring in ferromagnetism, the result being a dielectric analogy of the Curie point. As the rotating unit is only one of several factors in the lattice

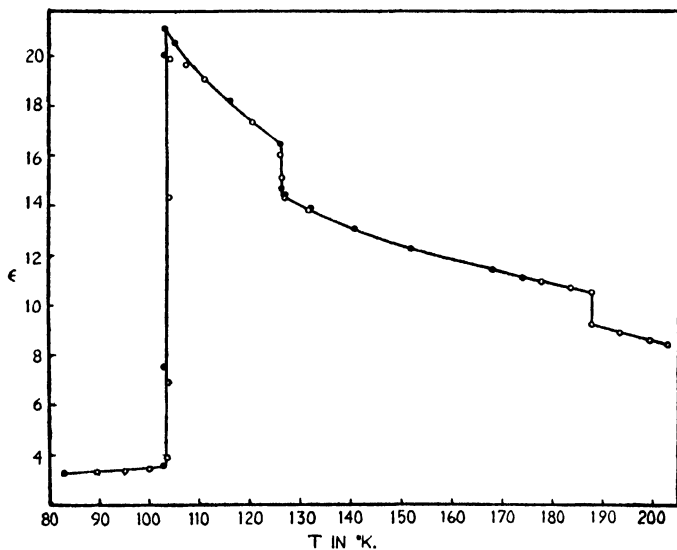


FIG. 6. Dielectric constant-temperature curve (at 5 kilocycles) of hydrogen sulfide: circles, rising temperature; dots, falling temperature.

of these hydrates, the crystal form may have a lower symmetry than in the cases of those substances in which the entire molecule is rotating.

Hydrogen sulfide is shown by its specific heat-temperature curve (13) to undergo two transitions in the crystal, which are checked within 0.1°C . by breaks in the dielectric constant-temperature curve (figure 6) (79, 49). This latter shows that freedom of molecular rotation occurs below the melting point and is practically unaffected by the higher transition, which is evidently only a minor lattice change; the rotation ceases abruptly below the lower transition, 103.5°K . At about this temperature x-ray analysis shows a cubic lattice, which presumably persists up to the melting point but is not necessarily the structure below the lower transition. Prelimi-

nary dielectric constant measurements (83) show that hydrogen selenide, which has a cubic lattice at about 103°K ., possesses freedom of molecular rotation in the crystal even at liquid air temperature.

Hydrogen fluoride resembles water and ammonia in that its specific heat-temperature curve shows no transition in the solid above liquid air temperature (14). X-ray and dielectric constant data are not available. Increase in the size of the halogen brings about molecular rotation in the

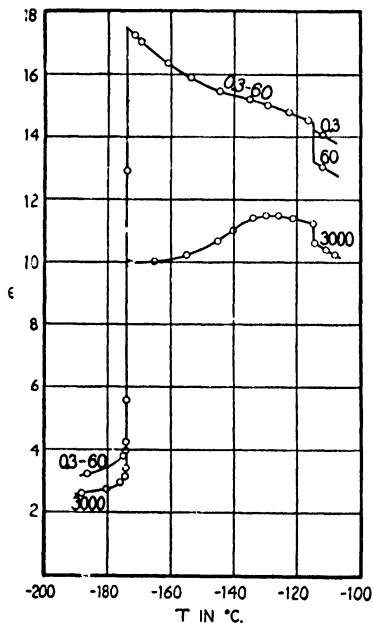


FIG. 7

FIG. 7. Temperature dependence of the dielectric constant (at indicated kilocycles) of hydrogen chloride.

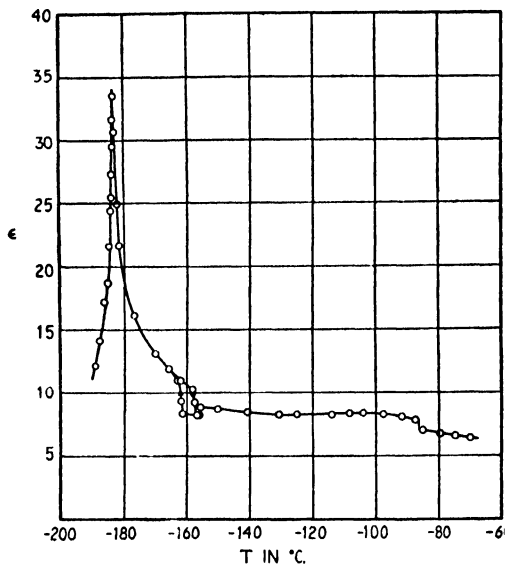


FIG. 8

FIG. 8. Temperature dependence of the dielectric constant (at 60 kilocycles) of hydrogen bromide.

crystal. Hydrogen chloride solidifies with a cubic lattice which has a dielectric constant (figure 7) (16, 80) higher than that of the liquid, increasing in accordance with the Debye equation as the temperature falls and dropping sharply to a low value as molecular rotation ceases at 98.9°K ., where specific heats (30, 37) indicate a rotational transition. Below this transition x-ray analysis shows orthorhombic symmetry and, for some degrees below it, the slowly diminishing dielectric constant and conductance, which latter rises sharply at the transition, indicate a very slight or

occasional but decreasing freedom of rotation. Hydrogen bromide (figure 8) resembles the chloride in showing rotation, but differs from it in possessing two additional transitions above that at which the lattice probably changes from orthorhombic to cubic with the setting-in of rotation. Because of disagreement between investigators (64, 70) the crystal structure is not certain, but the orthorhombic modification reported by Natta (64) in the neighborhood of the lowest transition probably corresponds to the lattice of non-rotating molecules, and the cubic lattice reported by him in the vicinity of the two upper transitions presumably consists of rotating molecules. Ruhemann and Simon (70), however, believe that the lattice is face-centered rhombic throughout. The two additional transitions are so close together that it can only be said that the dielectric constant (80) is slightly lower between them, but above them the dielectric constant-temperature curve is much flatter, showing a marked change in the internal field of the crystal. The lowest of the three transitions differs from all the others which are here discussed in that the dielectric constant rises very high and depends upon the frequency of the field in the immediate neighborhood of the transition. It appears that this may be a dielectric Curie point, a phenomenon previously observed only in Rochelle salt (25, 50, 93). Hydrogen iodide resembles the chloride and bromide in behavior, but differs from all the other simple molecules which rotate in the crystal in that it has a face-centered tetragonal lattice. The dielectric constant measurements have not been extended to the low temperature at which the specific heat indicates the commencement of rotation (39), but the one transition which occurs above this temperature causes a very slight drop in dielectric constant, followed by a much smaller rate of decrease in the dielectric constant with rising temperature. This transition evidently involves a change in the internal field, as in the case of the highest hydrogen bromide transition, but here also x-ray analysis shows no molecular rearrangement. Indeed, except for an abnormally large decrease in volume, presumably caused by the transitions, the lattice remains unchanged down to 21°K. (70), a temperature below the lowest transition. The temperature necessary to produce rotation decreases with increasing size of the halogen in this group of compounds, as it does in the ammonium halides. Increasing molecular size also facilitates rotation in the groups consisting of water, hydrogen sulfide and hydrogen selenide and ammonia, phosphine and arsine. The reverse is true in the case of methane and monosilane, where also the first member of the group rotates in contrast to the other three groups, in which the first member shows no rotational transition. All of these rotators except the ammonium ion, methane, and monosilane have dipoles, which decrease in size with increasing size of the molecule and are, at the same time, farther separated from one another

the larger the molecule. In both of these ways, therefore, increasing size of the molecule should facilitate rotation by decreasing the height of the potential energy hump which tends to prevent molecular rotation. In the ammonium halides the field due to the negative charge of the halide ion decreases with increasing ionic size, and the potential hump is thereby reduced. In all of these solids van der Waals forces are tending to draw the molecules or ions together, but the potential energies due to these forces should not vary greatly with orientation of the ions or molecules. The van der Waals forces must be greater in monosilane than in methane, because of the greater polarizability of the molecule (75). The variation in the resulting potential energies with molecular orientation may be sufficient to account for the higher rotational transition temperature of monosilane.

The energy changes (13) accompanying these rotational transitions seem not to show any very general relationships. The heats of fusion of the hydrides in which rotation occurs are much lower than those of ammonia, water, and hydrogen fluoride, since they have already acquired considerable amounts of energy before reaching the melting point.

The small molecule of hydrogen cyanide shows no molecular rotation in the solid according to recent dielectric constant measurements (83). It may be that the HCN molecules, which are linear, are so located in the lattice as to block one another's rotation, as do the I_2 molecules in their crystal. The large dipole moment, 2.93×10^{-18} (81), in the small molecule would give a strong internal field and a large variation in potential energy with orientation of the molecule, which would tend to prevent rotation. The x-ray photographs of potassium cyanide give no evidence of separate carbon and nitrogen positions, which would be expected if the cyanide ion were rotating in the lattice (90). It seems probable that the potential barrier to rotation of this ion is lower than that for the hydrogen cyanide molecule, so that rotation may occur.

In view of the ease of rotation of methane and of hydrogen chloride, bromide, and iodide, it is interesting to conclude from the low dielectric constant values found (60) for solid methyl chloride, bromide, and iodide that there is no molecular rotation around any axis perpendicular to the carbon-halogen line. The dielectric constant, of course, gives no information as to rotation around the carbon-halogen line, in which the molecular dipole lies. Low dielectric constants found (60) for solid methylene chloride and chloroform also give no evidence of molecular rotation. The dielectric constants of solid ethylene chloride (79), examined for intramolecular rotation as well as that of the molecule as a whole, and of solid nitromethane (85) show no rotation. It is probable that all of these molecules are so located in their lattices as to block one another's rotations

around axes perpendicular to the axes of symmetry in which the dipole moments lie. The dielectric constant of heptyl bromide shows no rotation, perhaps because of the low temperature at which it melts.

In methyl alcohol specific heat measurements show a transition a short distance below the melting point, and dielectric constant measurements show some freedom of rotation above this transition (79, 82). A new factor enters into the consideration of this rotation, for it might be a rotation of the entire molecule, as in the previous cases examined, or it might be merely a rotation of the hydroxyl group around the single carbon-oxygen bond, with which the dipole in the H—O makes an angle not far from 110° . If it is rotation of the hydroxyl group within the molecule, similar rotation should occur at least as easily and probably more easily in the higher aliphatic alcohols. As the specific heats which have been determined for higher aliphatic alcohols show no rotational transition, and as dielectric constant measurements (82) upon tertiary-butyl alcohol and *n*-octyl alcohol show that there is no dipole rotation in these solids, it must be the entire molecule which rotates in solid methyl alcohol. However, the dielectric constant is so much lower in the solid than in the liquid that the freedom of rotation is evidently much more reduced by the internal field of the solid than by that of the liquid. Possibly rotation occurs only about the C—O axis. Bernal (2) has found by x-ray analysis that dodecyl alcohol shows a transition from monoclinic to hexagonal at 289°K. with molecular rotation setting in around the axis of the carbon chain. It is probable that the higher temperature attainable before melting gives the necessary energy which was lacking in the case of the lower melting octyl alcohol.

Ethyl behenate, with its very long carbon chain and considerable dipole not far from one end of the chain, shows by its dielectric constant (9) that it possesses some freedom of rotation above a transition at 316°K. , which is only 4.8° below its melting point. The situation is complicated by the existence of two α -forms above this transition and two β -forms below it, with the possibility of metastable equilibrium. However, the polarizations of the α -forms are somewhat less than half way from those of the β -forms, which show no rotation, up to that for the liquid. Presumably, there is in the α -form some rotation about the axis of the long carbon chain like that in dodecyl alcohol and the long chain hydrocarbons previously mentioned.

Methyl sulfate (figure 9) shows a tremendous drop of 52 units in its dielectric constant on solidification at 241.7°K. , but the value 8 of the solid shows the persistence of some freedom of dipole orientation (78). The tendency of this value to increase slightly with falling temperature indicates sufficient freedom to permit of a partial conformation to the Debye

equation for the dielectric constant. This freedom disappears abruptly when the dielectric constant drops to 3 at about 203°K., which is to be regarded as a rotational transition. If the two $\text{CH}_3\text{—O}$ groups attached to the central sulfur atom were free to rotate around their sulfur-oxygen bonds, the dipoles associated with the C—O bonds might possibly account for the value of the dielectric constant between the melting point and the transition. However, it appears probable that the two methyl groups would collide frequently and interfere with one another's motion, and that their freedom of rotation might be hindered by the forces exerted upon them by the rest of the molecule. It seems more probable that, between

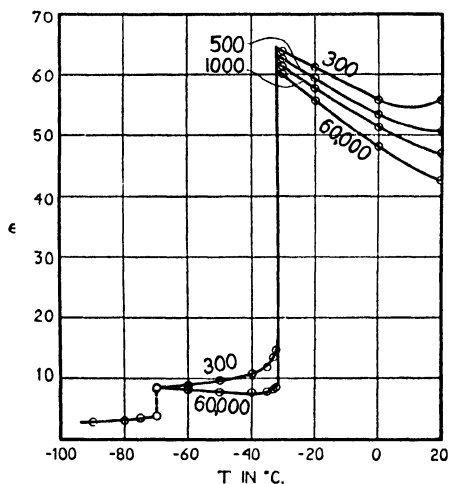


FIG. 9. Variation of the dielectric constant of dimethyl sulfate with temperature and frequency (in cycles).

the transition point and the melting point, the molecule is free to turn around an axis which makes an angle quite different from 90° with the axis of the effective dipole of the molecule as a whole. This means that only the component of the moment perpendicular to the axis of rotation, that is, $\mu \sin \theta$, where θ is the angle between the dipole axis and the axis of rotation, contributes to the dielectric constant in this region. The fact that ethyl sulfate (78) shows no molecular rotation indicates that the greater bulk of the ethoxyl group prevents either its rotation or that of the whole molecule, as the case may be.

The recent work of Morgan and his coworkers (88, 92) has shown that molecules bulkier than methyl sulfate may rotate in the solid. The dielectric constant of *d*-camphor hardly changes on solidification to a cubic

crystal at 450.7°K., and rises with decreasing temperature in the manner usual with a polar liquid. It is practically unaffected by a change from the cubic to a rhombohedral crystal at 370°K., but shows the disappearance of rotation from 236° to 233°K. when the crystals are transformed into very birefringent crystals, also rhombohedral. Molecular rotation persists in *dl*-camphor to a lower temperature, falling off rapidly below 208°K. and gradually for nearly 90° more. Borneol and isoborneol, which differ from camphor in possessing a CHOH group instead of a carbonyl group and, therefore, have a considerably smaller dipole moment, show rotation which ceases at a much higher temperature than in camphor. It is interesting to note that the mere interchange of the hydrogen and hydroxyl in the CHOH group changes the transition temperature 40° and causes a great difference in sharpness, isoborneol requiring about 35° and borneol about 5° for the major part of the change. Bornyl chloride, which has a chlorine instead of the hydroxyl of borneol, shows molecular rotation down to about 165°K. and *d*-camphoric anhydride shows it between freezing at 495°K., which lowers the dielectric constant but slightly, and a sharp transition at 408°K., where it ceases. The dielectric constant of cyclohexanol does not change on freezing, but falls off between 250°K. and 205°K., depending upon the frequency of the field, which shows that free rotation becomes difficult in this region and ceases below it. Other cyclohexyl compounds also are mentioned (88) as showing molecular rotation in the solid. The freedom of rotation of these large molecules is attributed by White and Morgan (88) to a loosening of the structure by great atomic vibration within the molecules, evidence of which is given by the large atomic polarization found for *d*-camphor. However, as the three dimensions of the camphor and related molecules do not differ greatly from one another, it is probable that the energies of many and, possibly in some cases, of all of the orientations of the molecule in the lattice differ from one another mainly in the energies of the molecular dipole in the field surrounding it. As the large hydrocarbon residues of the molecules presumably separate the dipoles widely, as compared to their spacing in a lattice of small molecules, they should lie in a comparatively weak field. It would appear, therefore, that molecular rotation should be possible without loosening by great intramolecular vibration. In the cyclohexane derivatives, it is easy to picture rotation occurring, at least around an axis perpendicular to the ring.

One might attribute the rotation in the borneols merely to the hydroxyl group in a molecule rigidly held in the lattice, but, as the other large molecules must rotate in order to account for their dielectric constants, there is no reason to suppose that the entire molecule does not rotate in the case of these hydroxyl compounds. Phenol, anisole, and hydroquinone di-

methyl ether, which were investigated by the dielectric constant method for possible rotation of the hydroxyl or methoxyl groups, show no molecular or group rotation in the solid. Dielectric constant measurements show no rotation in nitrobenzene and benzophenone; the latter was investigated because of its existence in different forms. As an entire benzene ring with attached group would have to rotate to be apparent in these measurements, it is natural to obtain a negative result. Aniline and methylamine also show no rotation of the molecule as a whole or of the NH_2 group around its carbon link. Ethyl ether, investigated because of the difference between its freezing and melting points (42), and acetone and succinic acid, which show small humps in their specific heat curves, give no evidence in their dielectric constant values of either molecular or group rotation (59). Indeed, dielectric constants have failed to establish definitely the existence of the free rotation of any group within a molecule in the solid state unless water of hydration is regarded as an intramolecular group. Specific heats are, however, sometimes interpreted as indicating group rotation within a molecule (66)

CONCLUSIONS

Of the eighteen substances of known crystal form in table 3 which show unrestricted ionic or molecular rotation, twelve, if potassium cyanide is included, are cubic when this rotation is occurring, four hexagonal, one, *d*-camphor, rotates freely both in its cubic and its higher temperature hexagonal form, and one, hydrogen iodide, is tetragonal, its *a*- and *c*-axes differing by only 8 per cent. The four which are only hexagonal are diatomic molecules rotating and melting at low temperature. Since free rotation gives spherical symmetry to a molecule, it is natural to find that molecules possessing it form lattices corresponding to the arrangements of close-packed spheres. When the axes of a molecule or ion are markedly different in length, rotation about only one of them, although tending to increase the symmetry, does not necessarily give rise to a cubic or hexagonal lattice.

It is evident that the moment of inertia of the molecule does not have the dominant effect in determining rotation that has been attributed to it in some discussions. The setting-in of rotation occurs at a higher temperature in monosilane than in methane, but this may be due to stronger intermolecular forces rather than to the larger moment of inertia of the molecule. The non-rotation of hydrogen fluoride and the very limited rotation in ice are due to hydrogen bonds between the molecules, or, possibly, merely to the strong internal fields in the crystals and the considerable dipole moments of the molecules as in ammonia. The heavier hydrides analogous to each of these three show rotation at lower temperatures with in-

creasing weights and, hence moments of inertia, probably because of the decrease in dipole moments with increase in size. The case of rotation of the camphor and similar molecules with very large moments of inertia shows that large moment of inertia in itself is not sufficient to prevent rotation. Actually, examination of Pauling's theory (66) shows that the moment of inertia is a factor in determining the oscillational or rotational energy levels of the molecule and, hence, the distribution of energy among the molecules, but does not directly affect the potential energy barrier which the molecule has to pass in order to rotate, except through its small effect in determining the zero energy level. It is this barrier which is all-important in determining rotation or non-rotation. If the molecule has a much larger moment of inertia around one axis than around the others, its rotation around this axis is more apt to be blocked by its shape. Increasing molecular size, incidentally involving increasing moments of inertia, gives greater potential energies between the molecules and, consequently, in most cases greater variation of potential energy with orientation of the molecule in the lattice or, in other words, greater potential barriers to prevent rotation. The shape of the molecule is one of the most important factors in determining these barriers, since upon it will depend largely their distance of approach in a rotational oscillation, and upon this distance primarily depends the intermolecular force. If the molecules do not actually block one another's rotation in the lattice, then the differences in the van der Waals forces exerted by different kinds of atoms and the size of the molecular dipole moment become important factors.

The setting-in of rotation may occur gradually because of the unequal distribution of energy among the molecules, as in borneol or in arsine, in which latter substance the transition, after a gradual start, ends with a sharp increase in rotation. Commonly, however, the transition accompanying the setting-in of rotation occurs almost as sharply as melting, because of the weakening of the intermolecular forces in the neighborhood of a molecule which has begun to rotate. In a number of cases a second transition occurs with little or no lattice change after rotation has set in with rising temperature, its only considerable effect upon the dielectric constant being a change in its variation with temperature, presumably as the result of change in the internal field. It is probable that, in some cases, rotation sets in at the lowest transition about one axis only, and that the higher transition involves the setting-in of rotation around another axis, as in the case of the nitrate ion in ammonium nitrate.

It has been previously mentioned that the energy changes accompanying the transitions of the hydrides seem to show no general relationships, although the heats of fusion of the hydrides with rotating molecules are much lower than those of the hydrides with non-rotating molecules. The

energy absorbed by a solid when molecular rotation sets in lies between 3 per cent and nearly 100 per cent of the heat of fusion. Commonly, the energy content of a solid with rotating molecules just below the melting point differs from that of the liquid just above the melting point by little, if any, more than it differs from that of the solid below the temperature where rotation sets in. From a molecular point of view, the essential difference between a solid with rotating molecules and a liquid is that the molecules of the solid are vibrating about points fixed in a lattice, while molecules of the liquid are vibrating about points which migrate slowly and irregularly through the liquid.

No attempt is made in the present discussion to consider solids containing more than one substance, except insofar as the effect of impurities is concerned. It is evident that non-polar molecular solids and most polar molecular solids have low dielectric constants arising principally from electronic displacements, while ionic solid dielectrics have higher, sometimes much higher, dielectric constants because of ionic displacements in addition to the electronic. A few polar molecular solids have molecules which are able to rotate within a considerable range of temperature, giving high dielectric constants over this range, and a few essentially ionic solids contain polar groups which can rotate and greatly increase the dielectric constant under certain conditions of temperature and frequency.

REFERENCES

- (1) AUSTIN AND PIERCE: J. Am. Chem. Soc. **55**, 661 (1933).
- (2) BERNAL: Nature **129**, 870 (1932).
- (3) BERNAL AND FOWLER: J. Chem. Physics **1**, 515 (1933).
- (4) BERNAL AND WOOSTER: Annual Reports of the Chemical Society (London) **1931**, 291.
- (5) BIJVOET AND KETELAAR: J. Am. Chem. Soc. **54**, 625 (1932).
- (6) BORN: Atomtheorie des festen Zustandes. Teubner, Leipzig (1923).
- (7) BRETSCHER: Trans. Faraday Soc. **30**, 684 (1934).
- (8) BRIDGMAN: Proc. Am. Acad. Arts. Sci. **52**, 91 (1916).
- (9) BUCKINGHAM: Trans. Faraday Soc. **30**, 377 (1934).
- (10) CLAUSIUS: Die Mechanische Wärmetheorie, Vol. II, p. 94. Vieweg (1879).
- (11) CLUSIUS: Z. physik. Chem. **3B**, 41 (1929).
- (12) CLUSIUS: Z. physik. Chem. **23B**, 213 (1933).
- (13) CLUSIUS: Z. Elektrochem. **39**, 598 (1933).
- (14) CLUSIUS, HILLER, AND VAUGHEN: Z. physik. Chem. **8B**, 427 (1930).
- (15) CLUSIUS AND PERLICK: Z. physik. Chem. **24B**, 313 (1934).
- (16) CONE, DENISON, AND KEMP: J. Am. Chem. Soc. **53**, 1278 (1931).
- (17) CRENSHAW AND RITTER: Z. physik. Chem. **16B**, 143 (1932).
- (18) DE BRUYNE AND SMYTH: J. Am. Chem. Soc. **57**, 1203 (1935).
- (19) DEBYE: Physik. Z. **13**, 97 (1912).
- (20) DEBYE: Polar Molecules, Chap. V. The Chemical Catalog Co., Inc., New York (1929).
- (21) DEBYE: Physik. Z. **36**, 100 (1935).

- (22) ERRERA: J. phys. radium [6] **5**, 304 (1924).
- (23) ERRERA: Bull. sci. acad. roy. Belg. **12**, 327 (1926).
- (24) ERRERA: Z. Elektrochem. **36**, 818 (1930).
- (25) ERRERA: Physik. Z. **32**, 369 (1931); Physik. Z. Sowj.-Union **3**, 443 (1933).
- (26) ERRERA AND BRASSEUR: Physik. Z. **34**, 368 (1933).
- (27) ERRERA AND SACK: Trans. Faraday Soc. **30**, 687 (1934).
- (28) EUCKEN: Verhandl. deut. physik. Ges. **18**, 4 (1916).
- (29) EUCKEN AND HAUCK: Z. physik. Chem. **134**, 161 (1928).
- (30) EUCKEN AND KARWAT: Z. physik. Chem. **112**, 467 (1924).
- (31) FOWLER: Proc. Roy. Soc. London **149**, 1 (1935).
- (32) FRENKEL, TODES, AND ISMAILOW: Acta Phys.-Chim. U. R. S. S. **1**, 97 (1934).
- (33) GIAUQUE: J. Am. Chem. Soc. **53**, 507 (1931).
- (34) GIAUQUE AND ASHLEY: Phys. Rev. **43**, 81 (1933).
- (35) GIAUQUE AND JOHNSTON: J. Am. Chem. Soc. **51**, 2300 (1929).
- (36) GIAUQUE AND STOUT: J. Am. Chem. Soc. **58**, 1144 (1936).
- (37) GIAUQUE AND WIEBE: J. Am. Chem. Soc. **50**, 101 (1928).
- (38) GIAUQUE AND WIEBE: J. Am. Chem. Soc. **50**, 2193 (1928).
- (39) GIAUQUE AND WIEBE: J. Am. Chem. Soc. **51**, 1441 (1929).
- (40) GRANIER: Compt. rend. **179**, 1314 (1924).
- (41) HENDRICKS, POSNJAK, AND KRACEK: J. Am. Chem. Soc. **54**, 2766 (1932).
- (42) HUETTIG AND SMYTH: J. Am. Chem. Soc. **57**, 1523 (1935).
- (43) HUGGINS: J. Phys. Chem. **40**, 723 (1936).
- (44) International Critical Tables, Vol. VI. McGraw-Hill Book Co., Inc., New York (1929).
- (45) JOHNSTON AND GIAUQUE: J. Am. Chem. Soc. **51**, 3194 (1929).
- (46) KAMERLING AND SMYTH: J. Am. Chem. Soc. **55**, 462 (1933).
- (47) KEESOM AND ONNES: Proc. Acad. Sci. Amsterdam **18**, 1247 (1916).
- (48) KELLEY: J. Am. Chem. Soc. **51**, 180 (1929).
- (49) KEMP AND DENISON: J. Am. Chem. Soc. **55**, 251 (1933).
- (50) KOBEKO AND KURTSCHATOV: Z. Physik **66**, 192 (1930).
- (51) KRACEK: J. Am. Chem. Soc. **53**, 2609 (1931).
- (52) KRACEK, BARTH, AND KSANDA: Phys. Rev. **40**, 1034 (1932).
- (53) KRACEK, HENDRICKS, AND POSNJAK: Nature **128**, 410 (1931).
- (54) KRACEK, POSNJAK, AND HENDRICKS: J. Am. Chem. Soc. **53**, 3339 (1931).
- (55) LATIMER AND HOENSHEL: J. Am. Chem. Soc. **48**, 19 (1926).
- (56) LIEBISCH AND RUBENS: Sitzber. preuss. Akad. Wiss., p. 211 (1922).
- (57) MAXWELL: Treatise on Electricity, Vol. II. Oxford (1881).
- (58) McALPINE AND SMYTH: J. Am. Chem. Soc. **55**, 453 (1933).
- (59) McNEIGHT AND SMYTH: J. Am. Chem. Soc. **58**, 1718 (1936).
- (60) MORGAN AND LOWRY: J. Phys. Chem. **34**, 2385 (1930).
- (61) MOSOTTI: Mem. soc. ital. Modena **14**, 49 (1850).
- (62) MÜLLER: Nature **129**, 436 (1932).
- (63) MURPHY: Trans. Am. Electrochem. Soc. **65**, 133 (1934).
- (64) NATTA: Gazz. chim. ital. **63**, 425 (1933).
- (65) PARKS: J. Am. Chem. Soc. **47**, 338 (1925).
- (66) PAULING: Phys. Rev. **36**, 430 (1930).
- (67) PAULING: J. Am. Chem. Soc. **57**, 2681 (1935).
- (68) RANDALL: The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids and Gases, Chap. V. John Wiley and Sons, Inc., New York (1934).
- (69) RUHEMANN: Z. Physik **76**, 368 (1932).

- (70) RUHEMANN AND SIMON: *Z. physik. Chem.* **15B**, 389 (1932).
- (71) SCHMIDT: *Ann. Physik* **9**, 919 (1902).
- (72) SIMON: *Ann. Physik* [4] **68**, 241 (1922).
- (73) SIMON: *Thermische Eigenschaften der Stoffe: Handbuch der Physik*, Vol. 10, Chap. 7. Julius Springer, Berlin (1926).
- (74) SIMON, SIMSON, AND RUHEMANN: *Z. physik. Chem.* **129**, 339 (1927).
- (75) SMYTH: *Phil. Mag.* **50**, 361 (1925).
- (76) SMYTH: *J. Am. Chem. Soc.* **51**, 2051 (1929); *J. Chem. Physics* **1**, 247 (1933).
- (77) SMYTH, ENGEL, AND WILSON: *J. Am. Chem. Soc.* **51**, 1736 (1929).
- (78) SMYTH AND HITCHCOCK: *J. Am. Chem. Soc.* **54**, 4631 (1932).
- (79) SMYTH AND HITCHCOCK: *J. Am. Chem. Soc.* **55**, 1296 (1933); **56**, 1084 (1934).
- (80) SMYTH AND HITCHCOCK: *J. Am. Chem. Soc.* **55**, 1830 (1933).
- (81) SMYTH AND McALPINE: *J. Am. Chem. Soc.* **56**, 1697 (1934).
- (82) SMYTH AND McNEIGHT: *J. Am. Chem. Soc.* **58**, 1597 (1936).
- (83) SMYTH AND McNEIGHT: *J. Am. Chem. Soc.* **58**, 1723 (1936).
- (84) SMYTH AND STOOPS: *J. Am. Chem. Soc.* **51**, 3312 (1929).
- (85) SMYTH AND WALLS: *J. Chem. Physics* **3**, 557 (1935).
- (86) SOUTHARD, MILNER, AND HENDRICKS: *J. Chem. Physics* **1**, 95 (1933).
- (87) STEARN AND EYRING: Paper presented before the Division of Physical and Inorganic Chemistry at the Ninety-second Meeting of the American Chemical Society, held in Pittsburgh, September, 1936.
- (88) WHITE AND MORGAN: *J. Am. Chem. Soc.* **57**, 2078 (1935).
- (89) WINTSCH: *Helv. Phys. Acta* **5**, 126 (1932).
- (90) WYCKOFF: *The Structure of Crystals*, p. 364. The Chemical Catalog Co., Inc., New York (1931).
- (91) WYMAN: *J. Am. Chem. Soc.* **53**, 3292 (1931).
- (92) YAGER AND MORGAN: *J. Am. Chem. Soc.* **57**, 2071 (1935).
- (93) ZELENY AND VALASEK: *Phys. Rev.* **46**, 450 (1934).

CONDUCTANCE, E.M.F., AND ACID-BASE CATALYSIS IN DEUTERIUM OXIDE

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An examination of the effects of deuterium substitution upon the properties of the oxide water discloses several interesting features. Those properties which are ordinarily classified as physical undergo as a rule less change on passing from the proto to the deutero form than do the properties which are classified as chemical. For example, the melting point of the waters is increased from 0° to $3.8^{\circ}\text{C}.$, or $+1.39$ per cent on the absolute scale of temperature; the boiling point $+0.39$ per cent; the latent heat of fusion $+6$ per cent; and the latent heat of evaporation $+2.5$ per cent.

On the other hand, it is not unusual for equilibrium constants to be increased or decreased three- to four-fold; i.e., the substitution of D_2O for H_2O as the solvent for the reaction produces effects which are roughly one hundred fold greater than are the effects upon purely physical properties.

A noteworthy exception is the viscosity. Here we find a decrease of 23.2 per cent on passing from H_2O to D_2O . Since the mobilities of the ions are determined primarily by viscosity, it is to be expected that the conductance of electrolytes will be reduced in corresponding manner.

Aside from the viscosity, the dielectric constant plays the dominating rôle in influencing the behavior of electrolytes, since this property determines the electrical free energy of the ions. The recent measurements of Horst Muller (14) and of Abadie and Champetier (1) indicate that the dielectric constants of D_2O and H_2O agree within 1 per cent. The dipole moments of H_2O and D_2O are identical. This fortunate circumstance permits a variation in viscosity without the complication of having the dielectric constant vary at the same time. In deuterium and protium oxides, nature has given us two single-component isodielectric solvents which are free from the objection which complicates the use of two-component isodielectric solvents; namely, that one component by virtue of its greater polarizability will be attracted to the neighborhood of an ion and the second component will be repelled from that neighborhood.

Table 1 summarizes the effects of deuterium substitution upon the acidic

dissociation constants of weak acids. Particularly striking is the sixfold decrease in the ion product of the solvent. It is natural to expect, therefore, that the kinetics of acid-base catalyzed reactions should exhibit

TABLE 1

The effect of deuterium substitution on the acidic dissociation constants of weak acids

$K \times 10^2$	VALUE IN		K_H/K_D	OBSERVER*
	H ₂ O	D ₂ O		
$H_3O^+ \rightleftharpoons H_2O + H^+$	55.5	55.4	~1	Calculated
Chloroacetic acid $\times 10^3$	1.7	0.6	3.	S.
Salicylic acid $\times 10^3$	0.97	0.25	3.8	K.
Acetic acid $\times 10^5$	1.84	0.58	3.2	C.
$NH_4^+ \rightleftharpoons NH_3 + H^+ \times 10^9$	5.5	2.0	2.3	S.
Hydroquinone $\times 10^{11}$	2.6	0.68	3.8	K.
$(H^+)(OH^-) \times 10^{14}$	1.00	0.16	6.2	A., B., and R.

* S. = Lewis and Schutz.

K. = Korman and La Mer.

C. = La Mer and Chittum.

A., B., and R. = Abel, Bratu, and Redlich.

TABLE 2

Effect of the substitution of deuterium for protium on reaction kinetics

REACTION	CATALYST	k_H/k_D	OBSERVER*
Nitroethane neutralization.....	OH ⁻	6.0	W. J.
Sucrose inversion.....	H ₃ O ⁺	0.5	G. S. S.
Ester hydrolyses.....	H ₃ O ⁺	0.67	W. J.
	OH ⁻	0.75	
Nitramide decomposition.....	H ₂ O	5.2	V. K. L. and J. G.
	H ₂ O	3.86	W. H. H. and V. K. L.
Mutarotation of glucose.....	H ₃ O ⁺	1.32	W. H. H. and V. K. L.
	Ac ⁻	2.50	W. H. H. and V. K. L.
	(Hac) ^o	2.2	W. H. H. and V. K. L.

* W. J. = Wynne-Jones.

G. S. S. = Gross, Suess, and Steiner.

J. G. = La Mer and Greenspan.

W. H. H. = Hamill and La Mer.

pronounced effects. Table 2 shows that not only are the kinetic effects surprisingly large, but they may be either positive or negative.

The first reaction involves the rate of neutralization of the pseudo-acid nitroethane by hydroxyl ion and by deuterohydroxyl ion. The successive stages of this reaction were investigated by Wynne-Jones, using conductance

titrations. His results indicate that the rate at which a deutron in the nitroethane molecule is donated to a base, like OH^- or OD^- , is six times slower than the rate at which a proton is donated to the corresponding base.

On the other hand, for the inversion of cane sugar—a reaction catalyzed exclusively by hydrogen ion—the rate is twofold faster in D_2O than in H_2O .

The various H^+ -catalyzed ester hydrolyses appear to give uniform values of 0.67; the alkaline hydrolyses give 0.75 for the ratio $k_{\text{H}}/k_{\text{D}}$. The solvent decomposition of nitramide exhibits a decrease of 5.2 fold on passing from H_2O to D_2O .

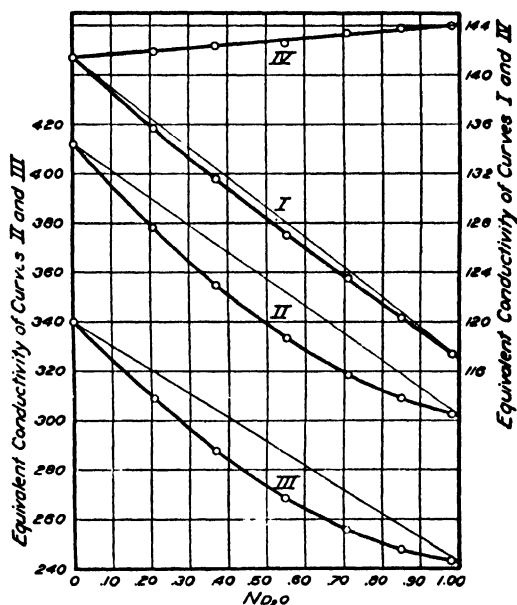


FIG. 1. Conductance data

The mutarotation of glucose is a reaction which is subject to multiple catalysis, but (by control of the pH and an accurate knowledge of the composition) it is possible to disentangle the effects of water, of H^+ ion, of basic ions (like acetate), and finally, even the catalysis due to the undissociated molecule of acetic acid, without ambiguity and with considerable precision, as shown recently (11) by Hamill and the author.

The interpretation of these acid-base catalyzed reactions requires an accurate knowledge of the dissociation constants of the acid-base systems involved. Since it is often impossible to obtain sufficiently large quantities of 100 per cent D_2O to carry out the kinetic measurements, it is necessary to resort to mixtures of D_2O and H_2O as the solvent.

An interesting question immediately arises. Are the kinetic and equilibrium constants sufficiently linear functions of the deuterium content of the solvent, so that it is safe to extrapolate data at intermediate concentrations to pure D_2O ? The answer in many cases is emphatically "No!" Both the kinetic and equilibrium-constant data frequently exhibit curves with marked sags.

Figure 1 summarizes the conductance data of Weldon Baker (3). Curve I for potassium chloride indicates an almost linear decrease in equivalent conductance with increasing deuterium content of the solvent. Paul Walden has for many years advocated the rule that the mobility of ions in different solvents, when extrapolated to infinite dilution, should be inversely proportional to the viscosity of the solvent; i.e., $\Lambda_0\eta = \text{constant}$. The Debye-Hückel-Onsager conductance equation yields the same result, provided that on passing from one solvent to another to vary the viscosity, the effective ionic carriers and their effective radii remain unchanged. H_2O and D_2O represent two ideal solvents for testing the Walden rule. Since their dielectric constants are identical, the ionic cloud effects should be identical at the same low concentration (0.01 M) in both solvents. Hence $\Lambda\eta$ should also be a constant at this concentration.

Curve IV shows that $\Lambda\eta$ for 0.01 M potassium chloride is not exactly constant but rises steadily from 141.4 to 144.0, or 1.93 per cent. In more recent work Chittum (13) has shown that precisely the same small linear increase holds for potassium acetate.

The cause of the small deviation from linearity in curve I (exhibited also by potassium acetate) is not certain. Fuoss suggests that the inconstancy of $\Lambda\eta$ may arise from a difference in the times of molecular relaxation of the two solvents, which time of relaxation is not adequately taken into account in the electrophoretic term of the Onsager equation. From a practical point of view it appears that sufficiently accurate values of Λ for salts at intermediate concentrations of H_2O - D_2O can be computed by linear interpolation of $\Lambda\eta$.

The situation is entirely different when we investigate the conductance of acids. Curve II shows that 0.01 M hydrochloric acid exhibits a very marked sag curve. A similar state of affairs holds for acetic acid, for the dissociation constant of acetic acid, and for the Walden product $\Lambda\eta$ for both acids (13).

A ready explanation (3) for the peculiar conductance of acids can be found in Born's theory (5) of hydrogen-ion conductance, which has recently been given a quantum-mechanical dress by Bernal and Fowler (4).

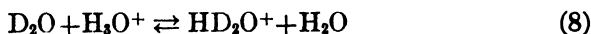
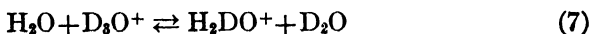
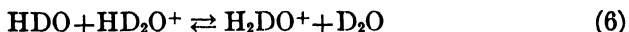
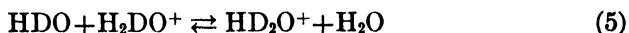
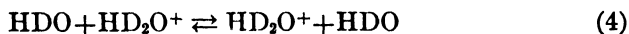
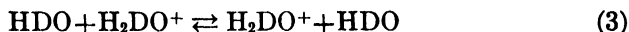
When an H_3O^+ ion is in sufficiently close contact with a water molecule, as in aqueous solutions, it need not retain its extra proton, since there is

another configuration of equal energy in which the extra proton has changed molecules, thus:



At any given time there is an equal probability of the proton being on either of the water molecules. However, if there is an applied field, F , the probability of the proton being found on one or the other of the water molecules is altered by an amount proportional to F , the migration of the proton being directed toward the region of lower potential energy.

The ions Cs^+ , Rb^+ , Th^+ , K^+ , NH_4^+ , Cl^- , Br^- , and I^- have about the same mobility in aqueous solutions, which is the maximum mobility of any ions except H_3O^+ and OH^- . The ordinary mobility of ions of the same charge is *primarily* a function of their effective ionic volume and not of their mass. The conductance of H_3O^+ is about five times that of the ions just mentioned. If the mechanism of conduction of H_3O^+ were the same as that of other ions, the radius, calculated on the basis of Stokes' law, would be absurdly small (2.6×10^{-9} cm.). According to the present view, the conductance of H_3O^+ must be considered as composed of two parts, (1) ordinary conduction similar to that shown by other ions, and (2) proton exchanges leading to a Grotthus chain type of conduction. In H_2O - D_2O solutions, in addition to proton exchanges between H_2O molecules, several other types of proton and deuteron exchanges are possible.



The symmetrical exchanges represented by equations 2, 3, and 4 are similar to equation 1 in having the same energy after the proton or deuteron transfer as before. On the other hand the unsymmetrical exchanges represented by equations 5, 6, 7, or 8 require an absorption of energy from, or an evolution of energy to, the surrounding medium. The frequency of the exchanges illustrated by equations 1, 2, 3, and 4 is all of the same order of magnitude, while the frequency of those illustrated by equations 5, 6, 7, and 8 will be less because of the necessity of exchanging energy simul-

taneously with the surrounding medium. At a concentration of 50 per cent D_2O , we have the maximum probability that an acid ion will not be next to a water molecule with which its extra proton or deuteron can exchange readily. In addition to this classical explanation there are also quantum-mechanical reasons for a lowered rate of transfer in equations 5 to 8.

In table 3 Λ^* refers to the Grotthus chain contribution obtained by subtracting the normal mobilities from the observed mobility Λ . It will be noted that although the fundamental picture presented by Bernal and Fowler is undoubtedly correct, their quantitative predictions fall wide of the mark.

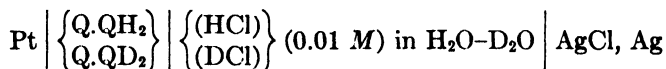
TABLE 3

	OBSERVED BY BAKER AND LA MER	PREDICTED BY BERNAL AND FOWLER
$\Lambda_{H^+}/\Lambda^*_{D^+} =$	268/182 = 1.48	20.
$\Lambda_{H^+}/\Lambda_{D^+} =$	339.8/242.4 = 1.48	5.

E.M.F. IN D_2O

When hydroquinone, QH_2 , is dissolved in D_2O the two phenolic protons¹ establish instantly an exchange equilibrium with the deutons of the solvent. It is only at high temperatures ($100^\circ C.$) and in alkaline media that the protons attached to carbon undergo a slow exchange (15). The quinhydrone ($Q.QH_2$) electrode by virtue of the rapidity of this exchange furnishes a means well adapted for studying exchange equilibria and the dissociation constants of acids in H_2O - D_2O mixtures.

Korman (12) has investigated the cell



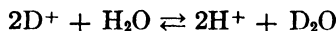
His results for $E | 0.01 M HCl |$ plotted against the deuterium content of the solvent are shown in figure 2. The E.M.F. in pure D_2O is 34.5 mv. higher than in H_2O . Most interesting is the appearance of a small but definite minimum value for 5 per cent D. Abel, Bratu, and Redlich (2) have investigated the cell



This cell also yields a minimum value for the E.M.F., but at about 40 mole per cent D. Table 4 gives a summary of the exchange equilibrium constants which may be calculated by combining both sets of measurements.

¹ Unpublished analyses by D. Price.

The exchange



exhibits the surprisingly large value $K = 15.30$. This unequal distribution of the acid ions is of considerable importance in interpreting the

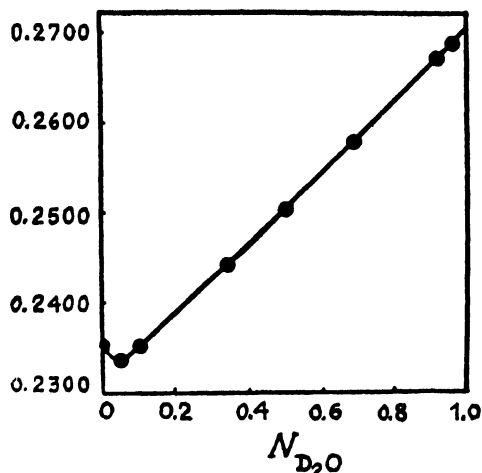


FIG. 2. Quinhydrone electrode in heavy water. $E_{0.01M HCl}$

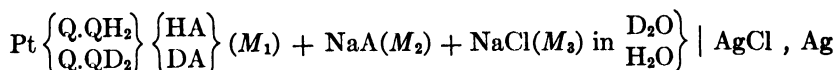
TABLE 4
Exchange equilibria in solution

NO.	PROCESS	$E^0 = \frac{RT}{F} \ln \frac{K}{(0.059/n)}$	K	OBSERVER
I	$2DCl + QH_2 = 2HCl + QD_2$	0.0345	14.64	L. and K.
II	$QH_2 + D_2O = QD_2 + H_2O$		0.96	H. and L.
III	$2DCl + H_2O = 2HCl + D_2O$	0.0034	15.30	I-II
IV	$2DCl + H_2(g) = 2HCl + D_2(g)$		1.30	A., B., and R.
V	$D_2(g) + H_2O = H_2(g) + D_2O$		11.80	III-IV
VI	$QH_2 + D_2(g) = QD_2 + H_2(g)$		11.26	I-IV
VII	$2H_2O + D_2(g) + 2NaOD = 2D_2O + H_2(g) + 2NaOH$	0.0431	28.58	A., B., and R.
VIII	$H_2O + 2NaOD = D_2O + 2NaOH$		2.42	VII-V
IX	$HCl + NaOD = DCl + NaOH$	0.0233	0.40	$\frac{1}{2}$ (VIII-III)
X	$2NaOD + H_2(g) = 2NaOH + D_2(g)$.21	VII-2V
XI	$D^+ + OD^- + H_2O = H^+ + OH^- + D_2O$		6.13	$\frac{1}{2}$ (VII + IV)

kinetic data of acid-base catalyzed reactions. K of reaction V, representing the exchange between the gases and the waters, is the square of the constant K'_3 employed by Farkas (7). Our E.M.F. value for $K'_3 = 3.44$ is

in excellent agreement with the averaged value of 3.36 obtained by previous investigators using analytical methods.

The E.M.F. of cells of the type



where A refers to the anion of a weak acid, permits one to calculate the dissociation constants of the weak acid in the H_2O - D_2O mixtures. The results are in agreement with those obtained by conductance (table 1).

KINETICS

When the relative velocities of sucrose inversion, catalyzed by hydrogen and deuterium ions in mixtures of H_2O and D_2O , as compared to the veloc-

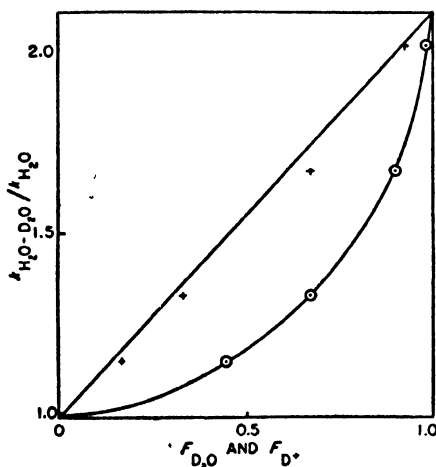
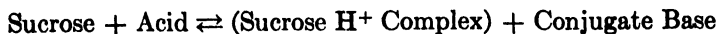


FIG. 3. Inversion of sucrose. O, $F_{\text{D}_2\text{O}}$; +, F_{D^+}

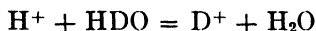
ity in pure water, are plotted against the fraction of D in the solvent, not only is a very marked sag curve obtained, but the rate is more rapid in D_2O (figure 3). Obviously the rate of this reaction is not proportional to the concentration of deuterium in the solvent; the explanation based upon the slower rate of proton as compared to deutron transfer offered for the neutralization of nitroethane is inadequate. Wynne-Jones (16) therefore suggested that the greater rate in D_2O requires an equilibrium of the type:



and a rate mechanism proportional to the dissociation of the sucrose ion.

It is possible to test this suggestion quantitatively (10) by assuming that the relative rates will be proportional to the relative deuterium- and hydrogen-

ion concentrations. In other words, a plot (crosses in figure 3) of the relative rate against the deuterium-ion concentration should yield a linear relation. The calculated value for the equilibrium constant for the reaction



for each kinetic measurement in the mixed solvent yields

$$K = 0.11, 0.12, 0.10, 0.14$$

Korman (12) has measured this equilibrium independently by electromotive force methods, and found a value of 0.14. The constancy and the agreement between the kinetically assumed and the independently measured values of this equilibrium constant furnish evidence that our interpretation is correct (10).

When a similar explanation is advanced for the now abundant data on the solvent catalysis of glucose mutarotation, Hamill (11) found that the kinetically computed and the experimentally measured values for the exchange constant between light and heavy glucose were $K = 0.84$ and 0.69 , respectively. The latter value refers to the geometric mean of the individual exchange constants of the five mobile hydrogens of glucose. It is to be expected that the kinetically determined values of K obtained from the equations

$$k_{\text{obsd.}} = k_{(\text{H}_2\text{O})} - (k_{\text{H}_2\text{O}} - k_{\text{D}_2\text{O}})F_{\text{DG}}$$

$$(\text{DG}) / (\text{HG}) = F_{\text{DG}} / (1 - F_{\text{DG}})$$

$$K = (\text{DG})(\text{HOH}) / (\text{HG})(\text{HDO})$$

would involve only the kinetically active hydrogen on the aldehydic group. The exchange constant for tetramethylglucose, which possesses only this one exchangeable hydrogen on the aldehydic group, was found to be $K = 0.83$ (9). The significance of this agreement is demonstrated by the close adherence of the velocity constants to the linear relationship when they are plotted against the fraction of heavy glucose F_{DG} rather than F_{D} of the solvent (figure 4).

The experimental data for the acetate ion, the hydrogen ion, and the molecular acetic acid catalysis of mutarotation are necessarily of lower precision. They can be described as linear within the experimental error, in respect to either F_{DG} or $F_{\text{D}_2\text{O}}$.

The important rôle which the kinetics of the decomposition of nitramide, $\text{H}_2\text{N}_2\text{O}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$, has played in the development of the modern concepts of acid-base catalysis, the remarkable obedience to a first-order rate equation, and the freedom from complicating side reactions—an ideal

behavior which is equally valid in heavy-water mixtures—make isotopic investigations of this reaction particularly significant. The reaction is not very sensitive to acid catalysis, but it is exceedingly sensitive to the presence of basic molecules. The catalytic minimum is broad. Between pH values of 2 to 5 it is flat. The substrate is a weak monobasic acid of dissociation constant 10^{-7} .

A semi-micro constant-volume gas evolution apparatus has been developed to investigate the reaction in D_2O (8). The results are as accurate (plus or minus 1 per cent) with 10 cc. of solvent as with the former macro apparatus, which required 100 cc. of solvent.

One is confronted with several possibilities for the mechanism of the reaction. The simplest assumption that only one form of substrate, pro-

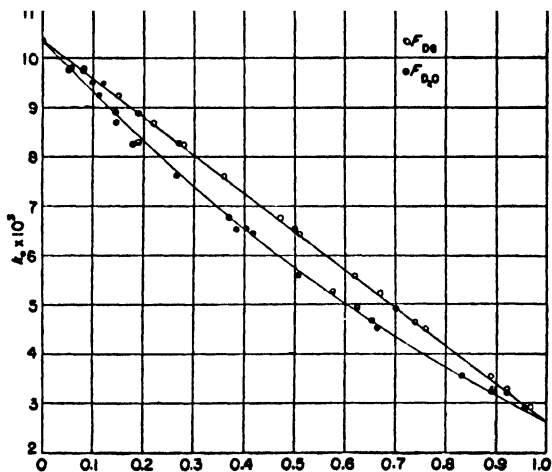


FIG. 4. Water catalysis in H_2O - D_2O at $24.97^\circ C$.

tonitramide, exists in the mixed waters and that this molecule undergoes a 5.2 fold slower rate of decomposition in D_2O than in H_2O can be eliminated on the grounds of the non-linear character of the curve and the acid properties of nitramide. A related mechanism extended to include the specific catalytic effects of HDO yields values of k_{HDO} which rise steadily. Hence this mechanism is improbable.

An equilibrium of the type



may be computed from the kinetic data in a manner analogous to that employed above for mutarotation. In terms of mechanism this scheme means that the velocity is determined entirely by the concentration of the

two forms of nitramide, the medium having no *direct* influence on the rate-determining step. Table 5 shows that the kinetically calculated values of

TABLE 5
Solvent decomposition of nitramide
(Measurements by Joseph Greenspan)

PER CENT D IN SOLVENT	10%	K_N	K'_N
4.69	1176.0	3.37	33.46
28.10	861.1	2.91	3.97
45.83	661.8	3.07	2.00
77.91	384.4	3.39	0.56
95.40	271.7	3.32	0.10
98.67	250.7	3.55	
		3.27 ± 0.2	

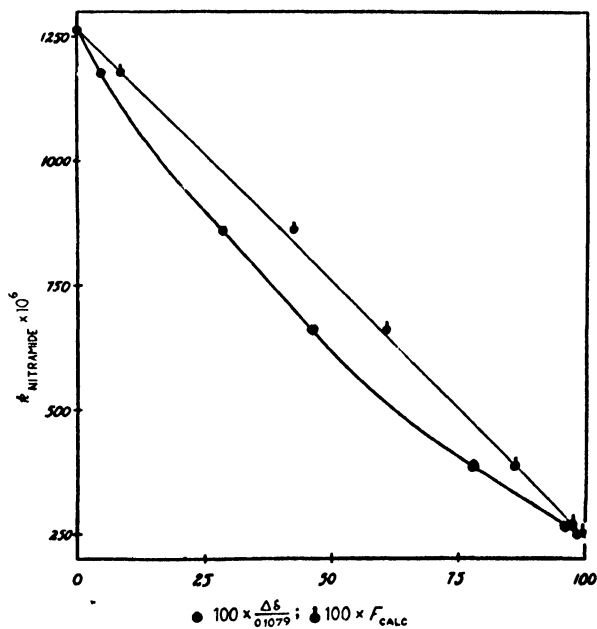


FIG. 5.

● k vs $100 \times \frac{\Delta\delta}{0.1079}$; ▲ k vs $100 \times F_{\text{calc}}$.

K_N are remarkably constant over the range of 4 to 99 per cent D_2O . The calculated value of the velocity constant, using the average value K_N

= 3.27, agrees with the observed values within experimental error as shown by the small deviations from the straight line in figure 5. Unfortunately the instability of nitramide has thus far prevented a direct determination of the exchange constant.

We have also tested the possibility that two protons are exchanged. The resulting exchange (K'_N) constant drifts violently, which we take as evidence that the exchange of one, and not two protons, is kinetically important. This result agrees with Pedersen's idea that the proton bound to nitrogen in the "aci" form is the one involved in the rate-determining step.

It appears from the data just cited that the displacement of the equilibrium of the isotopic exchange of the substrate or of the catalyst molecules with the solvent is an important factor in interpreting the kinetics in heavy-water mixtures.

REFERENCES

- (1) ABADIE, P., AND CHAMPETIER, G.: *Compt. rend.* **200**, 1387 (1935).
- (2) ABEL, BRATU, AND REDLICH: *Z. physik. Chem.* **173A**, 353 (1935).
- (3) BAKER, W. N., AND LA MER, V. K.: *J. Chem. Physics* **3**, 406 (1935).
- (4) BERNAL AND FOWLER: *J. Chem. Physics* **1**, 515 (1933).
- (5) BORN, MAX: *Z. Elektrochem.* **26**, 401 (1920); *Z. Physik* **1**, 221 (1920).
- (6) EUCKEN, JETTE, AND LA MER: *Fundamentals of Physical Chemistry*, p. 445. McGraw-Hill Book Co., Inc., New York (1925).
- (7) FARKAS, A.: *Light and Heavy Hydrogen*, p. 180 et seq. Cambridge University Press, London (1935).
- (8) GREENSPAN, LA MER, AND LIOTTA: *J. Am. Chem. Soc.*, in press.
- (9) HAMILL AND FREUDENBERG: *J. Am. Chem. Soc.* **57**, 1427 (1935).
- (10) HAMILL AND LA MER: *J. Chem. Physics* **4**, 294 (1936).
- (11) HAMILL AND LA MER: *J. Chem. Physics* **4**, 395 (1936).
- (12) KORMAN AND LA MER: *J. Am. Chem. Soc.* **58**, 1396 (1936).
- (13) LA MER AND CHITTUM: *J. Am. Chem. Soc.* **58**, 1642 (1936).
- (14) MÜLLER, HORST: *Physik. Z.* **35**, 1009-11 (1935).
- (15) MÜNZBERG, Z. K.: *Z. physik. Chem.* **177B**, 39-46 (1936).
- (16) WYNNE-JONES: *Chem. Rev.* **17**, 115 (1935).

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